1929

Studies in electrodialysis of soils

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STUDIES IN ELECTRODIALYSIS OF SOILS

By

Arthur Otto Alben

A Thesis submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major subject Soil Fertility

Approved

Signature was redacted for privacy.

In charge of Major work

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1929

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STUDIES IN ELECTRODIALYSIS OF SOILS

INTRODUCTION

Base exchange in soils has been studied to a considerable extent in recent years. As a result of these studies we now have a better insight into the formation and reclamation of alkali soils, the nature of soil acidity, the effects of fertilizer applications, and the mechanism of soil fertility in general. In short the results of base exchange investigations have enlarged our understanding of many fundamental soil problems.

Base exchange reactions in soils were discovered by Thompson (33) and Way (35) in 1850. Of base exchange or adsorption as he termed it, Way (35) said, "It may become a point of importance at a future time to ascertain how far the adsorptive power of a given soil bears relation to its known capabilities of bearing crops, and the principle may happily become available as a means of classification for soil."

Both parts of the foregoing prophecy have been fulfilled, at least in part. Gedroiz (11a) has recently suggested a system of classification of soils founded on their base exchange content and Rost (30), Humfeld (18), and others (19)(36) have studied base exchange in relation to soil fertility, and noted certain correlations.

The discovery of Thompson and Way attracted no special attention for more than half a century. It was brought to light and the whole subject of base exchange came to be studied extensively because of the work of Gedroiz of Russia, Hissink of Holland and Kelley and Brown of the United States.

The discoverers of base exchange in soils used various concentrations of salts as displacing solutions. Later workers have continued the use of salt solutions and have also employed weak solutions of acids and bases. More recently Mattson (28) used the H-ion liberated by means of electrodialysis as the displacing agent.

Salt solutions, weak acids, and alkalies have never made ideal displacing media. Solubility effects and side reactions take place to a greater or less extent. Leaching the soil with some of the more suitable solutions is a tedious and time consuming operation. Electrodialysis as a means of studying base exchange in soils gave promise of overcoming some of the objectionable features of the older methods. For this reason the following study was undertaken.

I. A STUDY OF THE METHOD

Literature Review

The principle of electrodialysis has found application in the past along various lines. Dhere and Gorgelewski (6), Adolf and Pauli (1), Bernhard and Beaver (3), Ettish and Beck (7), Freundlich and Loeb (9), and Pauli (29) have used electrodialysis on blood serums with various objects in view.

Bernhard and Beaver (3) used the apparatus shown in Figure I. It consisted of three pyrex tubes placed inside each other. The two smallest tubes had a membrane bottom consisting of cotton gauze covered with collodion. The positive electrode was suspended in the center chamber and the negative electrode was placed in the outer chamber. The electrodes were made of platinum foil. The whole apparatus was kept in a constant temperature bath during the process of electrodialysis.

Freundlich and Loeb (9) used a three chambered cell, as shown in Figure II. The three glass parts were ground to fit exactly on each other and could be fastened to a shaft for support. The center chamber held about 60 cc. The electrodes were circular pieces of platinum gauze placed next to the membranes which were made of parchment paper coated with chrome-gelatin. They employed a 12,

a 60, and a 120 volt direct current.

A cell similar to the one just described and shown in Figure III was used by Pauli (29). The cell was somewhat more complicated, however, as it provided for the passage of a flow of water through the outer chambers during dialysis. Parchment paper and collodion covered membranes were used. The anode was made of platinum gauze, the cathode of silver or iron. The apparatus was assembled in a vertical position and was placed in a horizontal position during operation.

Ettish and Beck (7) used a wool membrane covered with chrome-gelatin on the positive side and a parchment membrane on the negative side. The electrodes employed were brass on the cathode and platinum on the anode.

Lisbonne and Vielquin (25) and Friche et al (10) employed electrodialysis in the study of enzymes.

Friche, Fisher, and Barchus (10) used the stone-ware cell shown in Figure IV. The cell consisted of a number of pieces bolted together. The edges were polished and coated with a preparation of paraffin and rubber to make the cell water tight. The membranes used were made of a diaphragm covered with collodion prepared in glacial acetic acid. Chrome-gelatin was also used. A stirrer was placed in the compartment containing the material to be dialyzed. Steel wire was used for the cathode and synthetic

graphite for the anode.

Lisbonne and Vielquin (25) gave no description of their apparatus but stated that a collodion sac was employed for membrane and platinum for the electrodes.

Shepard, Sweet, and Benedict (31) studied gelatin by means of electrodialysis. They used a large wooden cell with outside dimensions of 75 cm length, 61 cm width, and 50 cm height. Inside of this cell was placed a smaller cell 36.7 by 35.5 by 36.7 cm made of Filtros, a porous silica septum, extending to and cemented to the bottom and sides of the wooden tank. The electrodes used were gold for the anode, 10.5 by 12.7 cm, and silver for the cathode 25.4 by 25.4 cm. The current used was 110 volts. The capacity of the cell was 48 liters.

Bechhold and Rosenberg (2) purified gelatin and glue by a process which they called ultrafiltration. The apparatus they used is shown in Figure V. The filtration was hastened by the application of an electric current in such a way as to have a tendency to exert a pull through the membrane. The rate of filtration was further increased by the application of suction. The cylinders, made of porous unglazed porcelain, were immersed in the solution. A collodion membrane was used. The anode was of platinum foil or a stick of carbon, while the cathode was of silver-plated material.

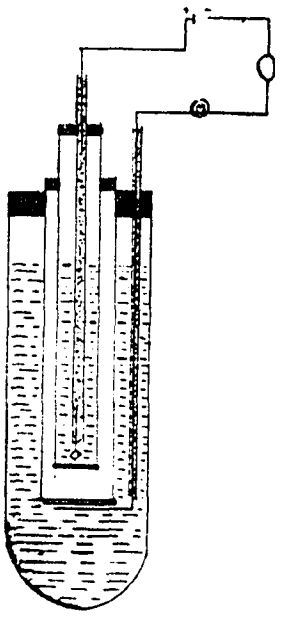

Fig. I

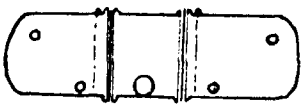

Fig. IIa

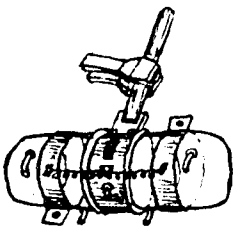

Fig. II b

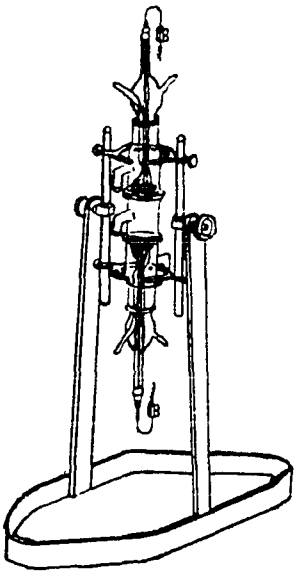

Fig. III

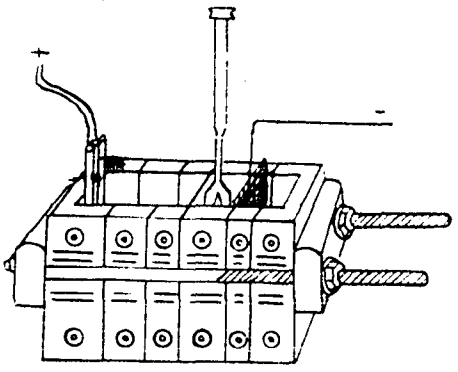

Fig. IV

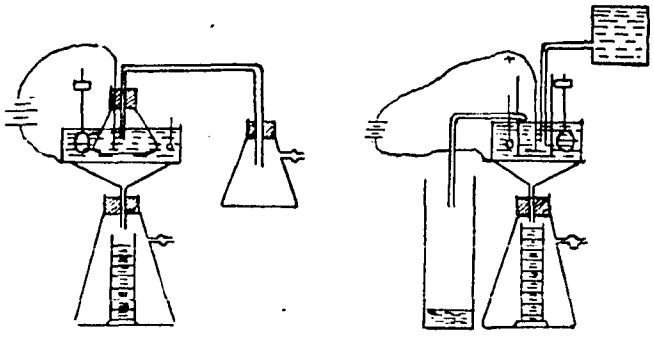

Fig. V

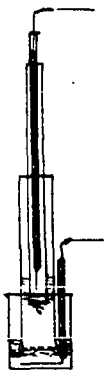

Fig. VI

Foster and Schmidt (8) used electrodialysis for the separation of the hexone bases from protein hydrolysates. Their cell consisted of a rectangular wooden box, 3 by 6 by 4.5 inches, which was cut into three approximately equal sections. The membranes separating the compartments consisted of strips of linen cloth coated with gelatin and fixed by allowing the strips to remain in formalin overnight. The whole was held together by means of bolts. Asphalt was used to waterproof the wood. Thin sheets of carbon were used for electrodes.

Taylor, Braun, and Scott (32) used the apparatus shown in Figure VI for the electrodialysis of insulin. Cloth treated with collodion was used for membranes.

Harvey (12) purified agar by electrodialysis, using the set up shown in Figure VII. The apparatus included a constant temperature bath in which was placed a large battery jar. The temperature was kept at 50°C. In the battery jar at opposite ends were placed two Electros Filtros cells and sufficient water added to almost cover the electrodes. A 110 volt current was used.

Hoffman and Gortner (16) also electrodialyzing agar, used a three-compartment box, each compartment of which had a capacity of 1250 cc. They were separated by heavy sheets of collodion supported by a double layer of white canvas. Carbon plates 12 by 15 cm were used for electrodes. The current was 220 volts D.C.

Loche and Hirsh (26) designed an apparatus for the electrodialysis of pseudo globulin. It consisted of two dialyzing thimbles, 16 by 100 mm, the upper end of each being closed with a three-hole rubber stopper. Two tubes were inserted for water circulation. A tube filled with mercury in which was sealed a platinum foil electrode, 1 by 4 cm, was placed in each thimble. The thimbles were mounted in a large cork stopper and placed in a beaker containing the material to be dialyzed. The thimbles were covered with parchment paper to prevent corrosion. Tap water was run continually through the tubes provided for that purpose. The details are shown in Figure VIII. This method, obviously, would not be adapted to soils work as no separation of the dialysates from the tap water is provided.

A series of experiments on the effect of an electric current on sludge obtained from water reservoirs was reported by Tillman (34) in 1907. The apparatus was not described, except that a process patented by Count von Schwerin was used. The author apparently was not interested in the composition of the solutions. However, he observed that when electrodialyzed a shrinking of the colloidal material took place.

Cameron and Bell (5) were the first workers in soils to use electrodialysis. In their study of the mineral constituents of the soil solution they used this method as

a means of removing the hydrolyzed products. They worked chiefly with finely powdered minerals, although in one case with a fine sandy loam soil.

Their apparatus, shown in Figure IX, consisted of two porous cups of unglazed porcelain, one fitted inside the other, and held in place by means of a rubber stopper. The outer cup, about 10 cm high by 45 cm internal diameter, was of the type commonly used in electric batteries. The inner cup was made by cutting off one end of a Pasteur-Chamberland filter tube. This cup was fitted with a rubber stopper carrying a block tin tube bent in a gooseneck form above the stopper and pierced with two holes directly below the stopper. These holes were provided to permit the escape and prevent the accumulation of gas in the inner compartment. The whole apparatus was placed in a beaker. The tin tube acted as the cathode and a strip of platinum foil as the anode. The current employed was 40 volts at first with a later increase to 80.

In 1911, Konig, Hasenbaumer, and Hassler (23), in an effort to determine the colloids in the soil, made use of the process of electrodialysis. No description of the apparatus was given, except that platinum electrodes were used. They stated that the amount of potassium found in the solution was about the same as can be extracted by hydrogen peroxide, and concluded that the adsorption of

phosphoric acid depends for the most part on the formation of insoluble calcium phosphate which is not brought into solution again by the action of an electric current. They were of the opinion that the process of electrodialysis could be recommended for the estimation of the soluble nutrients in the soil.

In 1913, Konig, Hasenbaumer, and Glink (22) used the apparatus shown in Figure X for the dialysis of soil and for the determination of its electrical conductivity. Parchment paper was placed underneath the soil, the space between the soil and the bottom receptacle being filled with distilled water. Platinum electrodes were placed at opposite ends of the soil mass. They concluded that the dialysis took too long a time for the process to be of practical application.

A continuation of the investigations of Konig, Hasenbaumer, and Hassler (23) was reported by Konig, Hasenbaumer, and Kuppe (24). The apparatus used previously was modified somewhat. It is shown in Figure XI. Two hundred grams of soil were placed in the cylindrical tube. Cork stoppers were inserted in such a manner that the soil was held in the center. Enough space was left to allow the percolation water to run off. Platinum discs were placed between the cork stoppers and the soil to serve as electrodes. Water was allowed to drip constantly on the water-saturated

soil, the runoff being collected in beakers. The current used was 220 volts D.C. If the temperature increased markedly, the voltage was decreased temporarily.

In order to determine the end-point of the solubility action of the electric current, the first two liters were analyzed separately. Apparently these workers did not consider the possibility of base exchange taking place. They concluded that similar amounts of potassium were brought into solution as were extracted by the hydrogen peroxide method, but that the quantity of phosphoric acid extracted varied so much that the method was scarcely applicable to laboratory research in soils.

Mattson (28) used the three-chambered cell shown in Figure XII. The center chamber, containing the material to be dialyzed, was separated from the two outside ones by parchment paper. Suspended in the solution in the two outside chambers were platinum gauze electrodes large enough to extend to the bottom of each chamber. The cell consisted of three pieces of U-shaped soft rubber separated by two sheets of parchment paper. The outside plates were made of hard rubber. The whole was fastened together by a number of bolts. The parchment paper was prevented from bulging by a glass lattice support. Outlets for the withdrawal of the dialysates were located at the bottom of each of the two

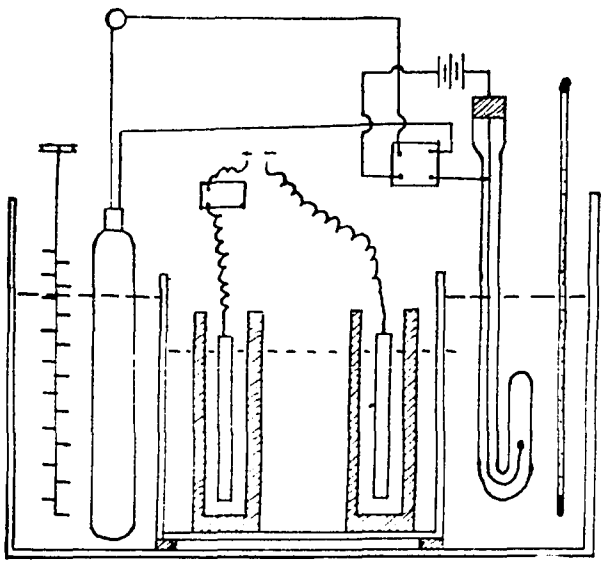

Fig. VII

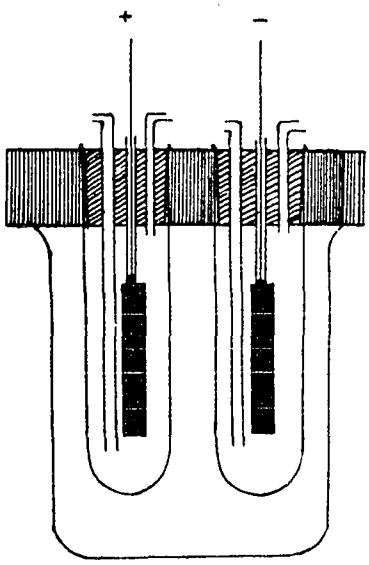

Fig. VIII

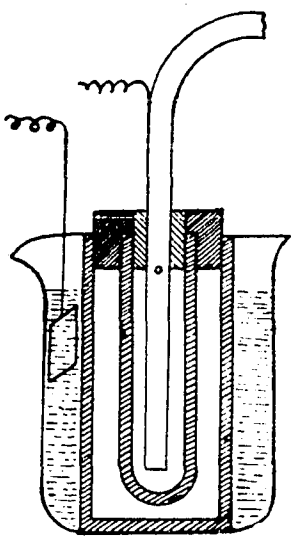

Fig. IX

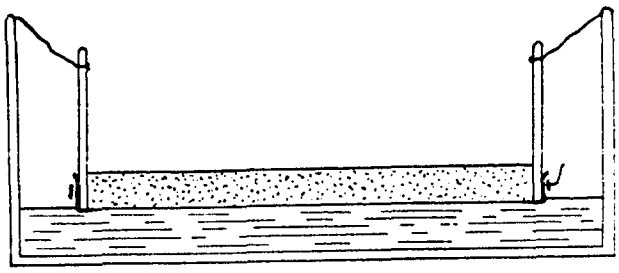

Fig. X

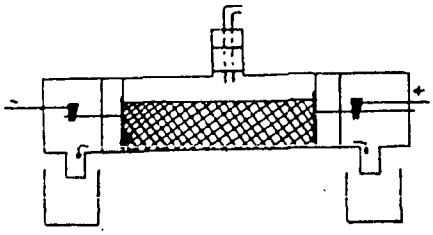

Fig. XI

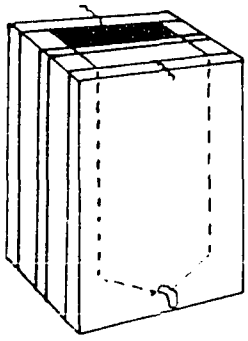

Fig. XII

outside chambers.

The literature reveals that various types of cells of varying proportions have been used for electrodialysis work. It is believed, however, that for soil studies the cell used by Mattson (28), shown in Figure XII, has the following advantages:

1. The soil layer is comparatively thin.
2. The distance between electrodes is short.
3. The dialysates are separated into acids and bases and can be conveniently collected for analysis.
4. The cell can be taken apart easily for cleaning and changing.
5. The capacity of the center chamber is such that it holds enough soil to give sufficient amounts of bases and acids in the dialysates for quantitative determinations.

A duplicate of the Mattson cell was used at the beginning of the following experiments. As the work progressed a few modifications were made.

Experimental

Changing the Dialysate

Parchment paper of the grade C. S. Co. 10040 was used as the dialyzing membrane. It was electrodialyzed for an hour before an experiment was started to remove salts. A 110 volt direct current was employed. A 25 watt lamp was used in series in the circuit to keep the temperature from rising above 50°C. The soil was a virgin Carrington loam obtained from the Agronomy farm of the Iowa Agricultural Experiment Station.

The bases obtained in the dialysate were titrated with HCl, using two indicators, phenolphthalein first, and when it became colorless adding methyl red and titrating with the same acid to the end-point. The acids were titrated with NaOH, using phenolphthalein as the indicator.

The results of an experiment with hourly changes for 56 hours and a total run of 139 hours are given in Table 1. The total amount of bases extracted is about 6 times the amount of acids extracted. The amounts of bases exceed the amounts of acids in each hourly extraction until at 36 hours when the acids amount to more than the bases.

The results of this experiment are graphically presented in Figure XIII. Both acid and base curves rise with a steep slope, change direction almost at right angles

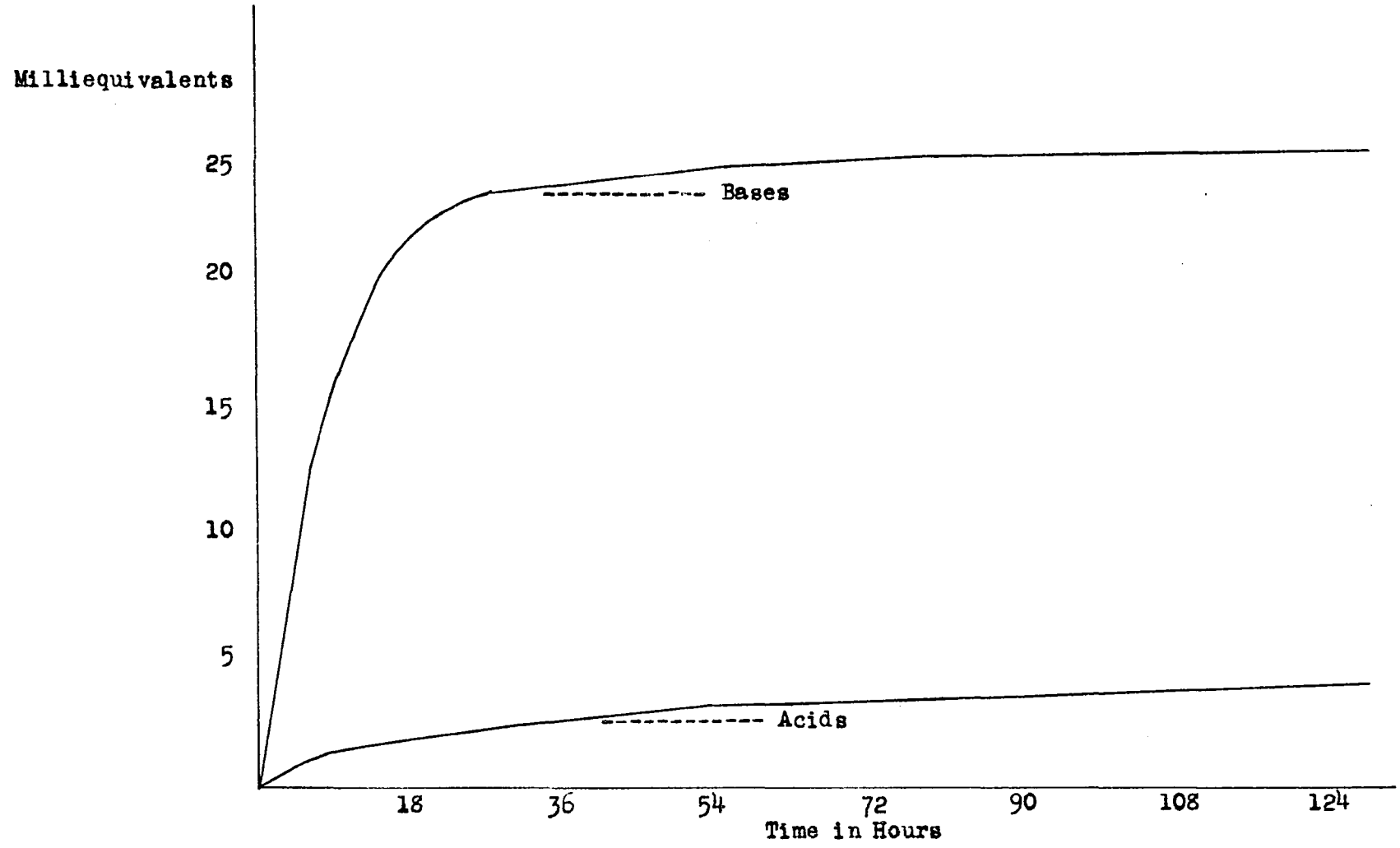

Figure XIII. Milliequivalents Extracted at Hourly Intervals

TABLE 1

Results With 1-hour Changes.

Change	Time between changes in hours	Temperature of center chamber °C.	Milliequivalents Acids in dialysates	Milliequivalents of Bases in Dialysates: With phenolphthalein as indicator	Milliequivalents of Bases in Dialysates: Additional with methyl red as indicator
1	1	37	0.436	2.486	-----
2	1	34	0.123	1.408	-----
3	1	35	0.134	1.709	-----
4	1	44	0.145	2.146	-----
5	1	42	0.156	2.825	-----
6	1	37	0.101	1.398	-----
7	1	37	0.112	1.379	-----
8	1	37	0.112	1.263	-----
9	1	40	0.134	0.777	0.214
10	1	36	0.067	0.825	0.214
11	1	36	0.067	0.515	0.408
12	1	37	0.067	0.437	0.340
13	1	37	0.056	0.262	0.757
14	1	37	0.067	0.233	0.437
15	1	35	0.056	0.175	0.388
16	1	37	0.045	0.146	0.369
17	1	36	0.033	0.136	0.320
18	1	36	0.033	0.029	0.311
19	1	36	0.033	0.010	0.301
20	1	37	0.033	-----	0.262
21	1	34	0.045	-----	0.243
22	1	33	0.022	-----	0.185
23	1	33	0.056	-----	0.146
24	1	33	0.056	-----	0.136
25	1	33	0.056	-----	0.126
26	1	34	0.067	-----	0.097
27	1	34	0.045	-----	0.087
28	1	33	0.043	-----	0.068
29	1	34	0.033	-----	0.068
[illegible]	1	[illegible]	0.045	[illegible]	[illegible]

23	1	33	0.056	-----	0.146
24	1	33	0.056	-----	0.136
25	1	33	0.056	-----	0.126
26	1	34	0.067	-----	0.097
27	1	34	0.045	-----	0.087
28	1	33	0.043	-----	0.068
29	1	34	0.033	-----	0.068
30	1	35	0.045	-----	0.058
31	1	34	0.033	-----	0.058
32	1	35	0.033	-----	0.058
33	1	35	0.033	-----	0.048
34	1	34	0.045	-----	0.058
35	1	34	0.045	-----	0.048
36	1	33	0.045	-----	0.039
37	1	32	0.056	-----	0.048
38	1	32	0.033	-----	0.039
39	1	32	0.045	-----	0.039
40	1	32	0.033	-----	0.039
41	1	32	0.045	-----	0.039
42	1	32	0.045	-----	0.029
43	1	30	0.033	-----	0.029
44	1	30	0.033	-----	0.029
45	1	30	0.033	-----	0.029
46	1	30	0.022	-----	0.019
47	1	35	0.033	-----	0.010
48	1	33	0.033	-----	0.019
49	1	33	0.033	-----	0.019
50	1	36	0.033	-----	0.029
51	1	38	0.033	-----	0.029
52	1	33	0.033	-----	0.019
53	1	32	0.033	-----	0.019
54	1	32	0.033	-----	0.029
55	1	31	0.033	-----	0.019
56	1	32	0.033	-----	0.019
57	11	48	0.045	0.116	0.107
58	6	40	0.067	-----	0.078
59	6	41	0.056	-----	0.048
60	12	44	0.134	0.048	0.058
61	4	42	0.056	-----	0.048
62	9	42	0.089	0.039	0.039
63	11	42	0.120	0.029	0.068
64	12	30	0.123	0.019	0.048
65	12	49	0.112	0.019	0.087

36	1	33	0.045	-----	0.039
37	1	32	0.056	-----	0.048
38	1	32	0.033	-----	0.039
39	1	32	0.045	-----	0.039
40	1	32	0.033	-----	0.039
41	1	32	0.045	-----	0.039
42	1	32	0.045	-----	0.029
43	1	30	0.033	-----	0.029
44	1	30	0.033	-----	0.029
45	1	30	0.033	-----	0.029
46	1	30	0.022	-----	0.019
47	1	35	0.033	-----	0.010
48	1	33	0.033	-----	0.019
49	1	33	0.033	-----	0.019
50	1	36	0.033	-----	0.029
51	1	38	0.033	-----	0.029
52	1	33	0.033	-----	0.019
53	1	32	0.033	-----	0.019
54	1	32	0.033	-----	0.029
55	1	31	0.033	-----	0.019
56	1	32	0.033	-----	0.019
57	11	48	0.045	0.116	0.107
58	6	40	0.067	-----	0.078
59	6	41	0.056	-----	0.048
60	12	44	0.134	0.048	0.058
61	4	42	0.056	-----	0.048
62	9	42	0.089	0.039	0.039
63	11	42	0.120	0.029	0.068
64	12	30	0.123	0.019	0.048
65	12	49	0.112	0.019	0.087
				Sub Totals 18.420	7.011
Total	139		4.321	Total M.E. of Bases 25.431	

in a few hours time and then assume a straight line. The sudden break in the base curve indicates that the exchange bases are extracted with a rather definite end-point, after which slight solubility effects come into play.

As it is rather inconvenient to change solutions every hour, it was thought that it might be possible to allow a longer period of time to elapse between changes, accordingly the time of dialysis was extended to 6- and 12-hour intervals. The results are shown in Table 2.

Another exporiment was run using time intervals of 1-hour, 1-hour, 4-hours, and 12-hours. The results are shown in Table 3.

The results of these two experiments show that the quantity of bases extracted is to some extent dependent on time. Lengthening the time interval between changes raised the temperature considerably, especially with a longer time interval near the beginning of the experiment.

Figure XIV shows the comparative rate of extraction with the various time intervals between changes. The rate of extraction is greatest with the hourly changes but all reach the same end-point in a reasonable length of time. The smaller volume of dialysate handled and the fewer changes made are points in favor of the longer change interval which make it more desirable than the hourly change.

An attempt was made to complete the dialysis

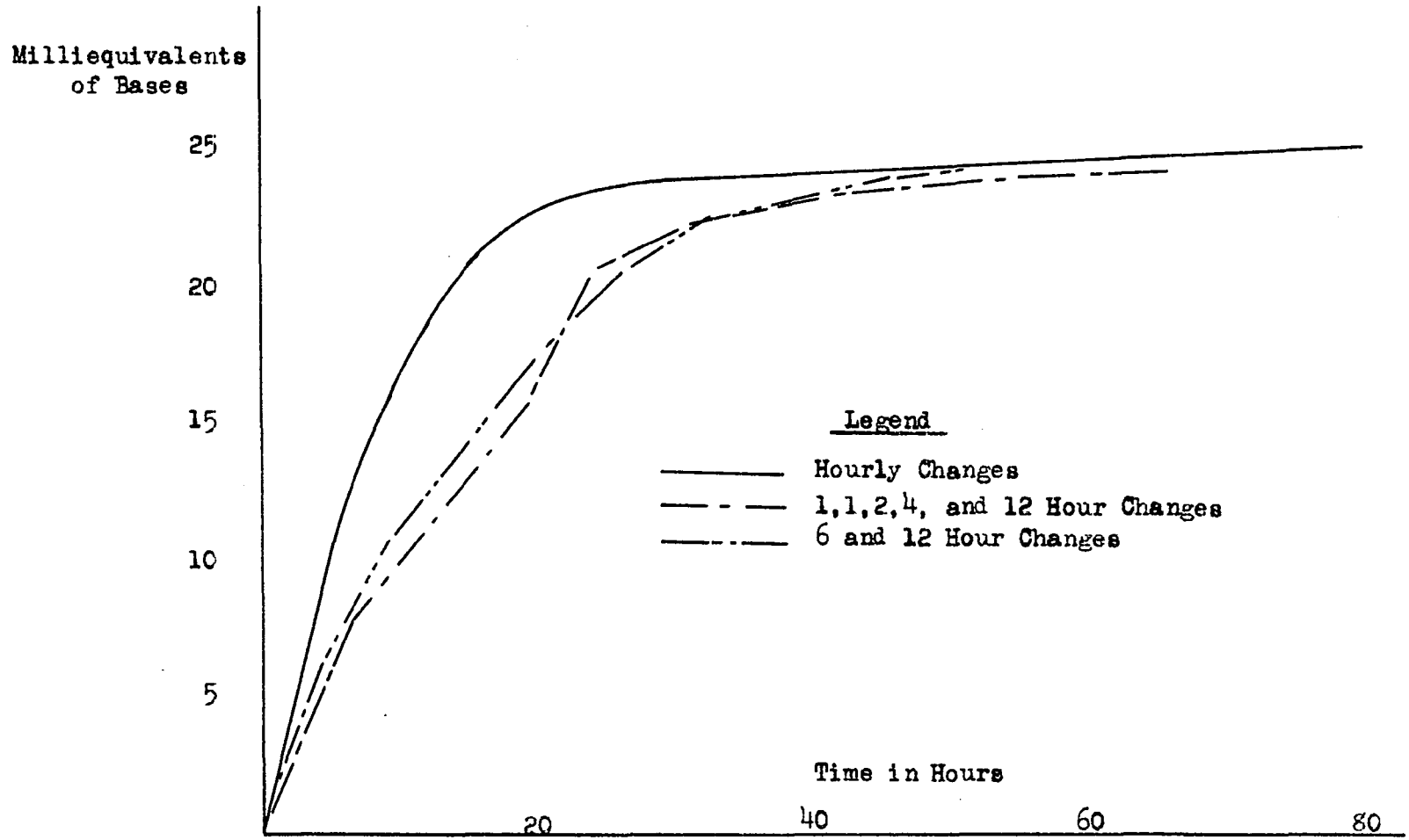

Figure XIV. Effect of Varying Time Changes

T A B L E 2

Results of 6 Hour and 12 Hour Changes.

Time in hours	Temperature in degrees C.	M. E. bases	M. E. acids
6	50	7.65	1.28
18	50	7.85	0.72
24	51	5.13	0.35
30	42	1.74	0.13
42	40	1.00	0.13
54	40	0.29	0.12
66	39	0.13	0.07
	Total	23.79	2.80

TABLE 3

Results of 1 Hour, 1 Hour, 2 Hour, 4 Hour, and 12 Hour Changes.

Time in hours	Temperature in degrees C.	M. E. bases	M. E. acids
1	31	1.58	0.29
2	32	1.61	0.22
4	35	3.10	0.19
8	35	4.28	0.26
20	34	6.70	0.49
26	40	3.26	0.16
32	41	1.89	0.19
44	40	1.45	0.17
54	37	0.30	0.08
	Total	24.17	2.06

without changing the solutions in the cell. This attempt was unsuccessful as it appears that a maximum concentration is reached in the dialysates after about three or four hours, and no appreciable increase in the quantity of bases is obtained with the first change at a longer period. Further experiments indicate that changes at 3, 6, and 12 hour intervals give satisfactory results, and that when Carrington loam is used an end-point is reached in about five changes, a total time of 45 hours being required.

Change of Voltage

Since in many laboratories 110 volt direct current is not available, it was thought that a comparison of the results obtained with 110 volts D. C. with those secured at a lower voltage would be of interest and value. Therefore, a small rectifier rated at 7.5 to 15 volts operated by 110 volts A. C. was used. The results are shown in Table 4.

The data obtained show that the bases and acids are being removed at too slow a rate for this method to be of practical value for the determination of total replaceable bases. When compared with the results obtained with 110 D. C., it will be seen that the end-point has not been reached at the end of 143 hours. Furthermore, the slowing

TABLE 4

Results with 7.5 to 15 Volt Rectifier.

Time in hours	Temperature in degrees C.	Ammeter reading in amperes	M. E. bases	M. E. acids
10	27	0.08	2.93	0.44
16	24	0.06	1.50	0.09
22	23	0.03	1.13	0.09
35	28	0.08	3.36	0.21
46	31	0.08	4.54	0.33
59	26	0.04	1.56	0.07
69	28	0.03	1.13	0.06
83	30	0.03	0.88	0.04
93	30	0.02	1.04	0.05
107	27	0.02	0.54	0.04
117	27	0.02	0.65	0.04
131	27	0.02	0.51	0.03
143	28	0.02	0.19	0.04
		Total	19.96	1.53

down of the rate indicates that the time required for complete removal of bases would be excessive.

Better results were obtained by connecting a one-eight hourse power A. C. motor to a one-eight horse power D. C. motor reversed. This hookup gave between 50 and 55 volts. The rate of dialysis compared favorably with the rate obtained with 110 volts D. C. The temperature remained lower and a rather definite end-point was obtained. Table 5 shows the detailed data.

It would seem that if the equipment mentioned is available reasonably satisfactory results may be expected, but if equipment must be bought it would be preferable to buy a higher voltage outfit.

Cooling

Temperature control would seem to be desirable if by such means solubility effects could be reduced to a minimum. Mattson endeavored to keep down the temperature in the cell by means of a 25 to 50 watt lamp in series. The same means were used in these experiments. However, it was observed that at times the temperature would rise as high as 50°C.

In order to control the temperature more effectively, the following modification of the cell was made. The

T A B L E 5

Results with 1/8 h.p. A. C. Motor and

1/8 h.p. D. C. Motor Reversed.

Time in hours	Temperature in degrees C.	Ammeter reading in amperes	M. E. bases	M. E. acids
2	27	0.09	1.14	0.31
4	28	0.07	1.48	0.11
8	29	0.09	3.01	0.42
12	30	0.09	3.45	0.26
25	30	0.10	5.40	0.31
29	35	0.16	3.57	0.22
36	44	0.19	4.19	0.42
48	36	0.08	1.52	0.31
52	32	0.05	0.30	0.14
		Total	24.06	2.50

lattice of glass rods on each side of the parchment paper was replaced by two thin glass tubes bent in the shape of a grid. The grids were connected to the water system by means of rubber tubing, and cold tap water was run through them continuously. The temperature was kept between 18° and 22°C. by this means.

Later, another grid was placed in the center compartment containing the soil, thereby eliminating any possibility of excessive temperature in the soil itself. This method of cooling makes it possible to eliminate the lamp from the circuit. In almost all subsequent work this system of cooling has been successfully employed.

While it would seem desirable to keep the temperature of the cell controlled there did not seem to be any data available as to what would result if the temperature was not controlled. To throw light on this point an experiment was run without a cooling system and with no resistance in the circuit. A 110 volt D. C. current was used. The results of this experiment are shown in Table 6.

The time of changing solutions was rather irregular, due to increase of temperature. The boiling point was reached 35 minutes after the start of the dialysis. The solutions were changed at this time. The second change was made 1 hour and 15 minutes later, at which time the solutions were again boiling. After this change the temperature was

TABLE 6

Results With Cathode of Copper Gauze and Anode of Platinum Gauze Without Cooling System.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
35 min.	1.80	99	0.49	4.71
1 hr. 50 min.	1.13	99	0.42	3.55
3 hrs.10 min.	0.80	80	0.26	1.94
5 hrs.30 min.	0.60	81	0.25	1.13
9 hrs.	0.50	79	0.22	0.59
21 hrs.	1.00	60	1.51	3.60
		Total	3.15	15.52

high but did not again reach the boiling point.

The titrations show that in spite of the increase in temperature the usual amount of replaceable bases was obtained. However, on the acid side, there seemed to be considerable increase in solubility, the quantity of acids being approximately three times as great as when the cooling system was used. After all of the replaceable bases had been obtained, continued dialysis might have caused an increase on the basic side as well due to solubility effects. The forced time of changing due to the boiling temperature reached and the uncertainty of the time interval of changing were undesirable features of the experiment. The experiment was discontinued after 21 hours as the results showed the need of a cooling system.

Choice of Indicator

In Table 1 the milliequivalents of bases detected with phenolphthalein as indicator are given and also additional bases detected with methyl red as indicator. The amounts are 18.42 milliequivalents for phenolphthalein and 7.01 additional for methyl red. Later it was found that if the neutral point of phenolphthalein was taken as the end-point hourly changes would reach that end-point in a shorter time than changes at longer intervals. In other words, enough bases had not accumulated in an hours dialysis

to give a basic reaction with phenolphthalein, yet, appreciable amounts of bases would be detected with methyl red.

As shown by analyses, reported later, the first two changes with the 3 and 6 hour intervals contain calcium and magnesium and not much of anything else. Almost all of the calcium and magnesium would be detected with the phenolphthalein end-point. However, the later changes are made up largely of manganese, aluminum, and iron. Only small amounts, if any, of these bases are detected with phenolphthalein as the indicator but they are detected with methyl red. For this reason it would seem that the methyl red end-point is the better one to use in order to obtain the amount of bases extracted.

Some difficulty was experienced with the adsorption of methyl red. Less difficulty was had if an excess of acid was added and the solution then back titrated with sodium hydroxide. This procedure is almost necessary anyhow in order that the bases go into solution rapidly. Titration was found to be much easier immediately after changing solutions than after they had stood for a time. The bases form carbonates which are not as soluble as the hydroxide form found at the time of withdrawal of the dialysates from the cell.

Description of Apparatus

The cell previously described was modified from time to time. A description of the cell used in later experiments follows. The dimensions are shown in Figure XV.

The cell is three chambered. B_1 and B_2 are two pieces of soft plate rubber and A_1 and A_2 are U-shaped pieces of iron 1/8 inch thick and 1 inch wide. At H are holes for the 1/4 inch bolts which hold the pieces together. O is an opening for draining the cell. A glass stopcock may be inserted to facilitate the changing of solutions. E_1 and E_2 are 52-mesh platinum gauze electrodes 4 by 6 inches in size. The bolts are provided with wing nuts for convenience in taking the cell apart for cleaning. F_1 and F_2 are parchment paper membranes.

Summary

1. Electrodialysis of soils seems to be a promising method for studying the problem of base exchange.

2. Changing the dialysates at 3, 6, and 12 hour intervals was found to be satisfactory both as to convenience and rate of extraction.

3. The use of a rectifier, capable of delivering a maximum of 15 volts D. C. was found to give too slow a rate of dialysis for practical purposes. A motor generator

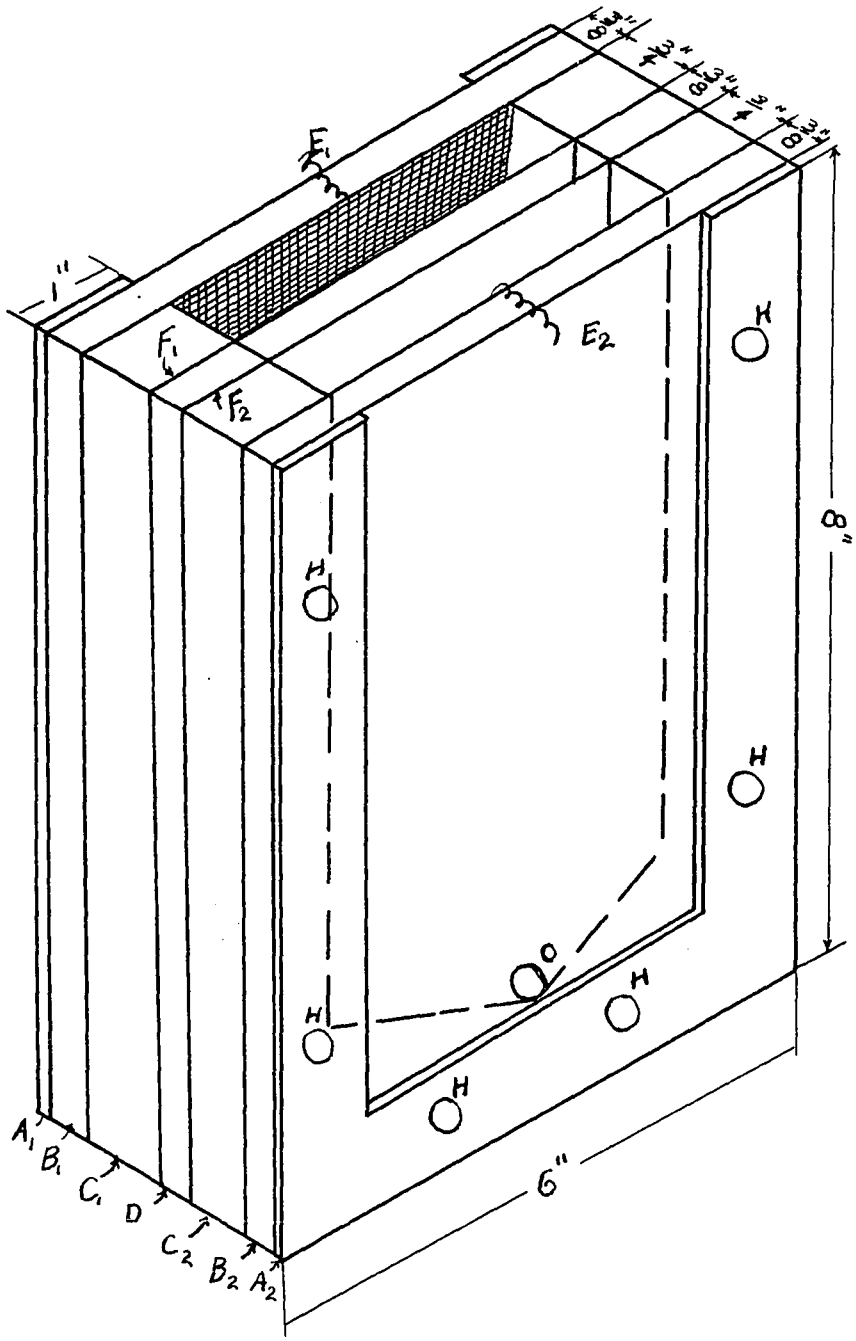

Figure XV Apparatus for the Electrodialysis of Soils

delivering 50 to 55 volts was found to give satisfactory results.

4. Temperature control was effected by means of a cooling system.

5. In the determination of total replaceable bases by titration of the dialysate, methyl red was found to be preferable to phenolphthalein as the indicator.

II. CHOICE OF ELECTRODES

Mattson (28) used platinum gauze electrodes in his work. As the cost of these electrodes is considerable, it would seem that if some cheaper material could be substituted for platinum, electrodialysis might come into more general use in soil work than would otherwise be the case. The results secured by the use of various substitutes for platinum follow.

Experimental

All the experimental data reported here on the use of different electrodes were obtained with the use of the modified Mattson cell as described previously. The soil used was a virgin Carrington loam obtained from the Agronomy Farm of the Iowa Agricultural Experiment Station. The solutions in the outer chambers were changed at the successive intervals of 3 hours, 6 hours, 12 hours, 12 hours, and 12 hours. At each change, a record was made of the time, the voltage, the amperage, and the temperature. An effort was made to keep the voltage between 110 and 120. In order to have a basis of comparison the first electrodes used were of platinum gauze 4 by 6 inches in size. The results of this experiment are shown in Table 7.

In the second experiment a trident-shaped platinum electrode was substituted for the platinum gauze

TABLE 7

Results With Cathode of Platinum Gauze

and Anode of Platinum Gauze.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	0.67	24	0.45	9.65
9	0.21	21	0.17	3.02
21	0.21	21	0.18	2.01
33	0.10	19	0.13	0.48
45	0.10	20	0.10	0.28
		Total	1.03	15.43

on the basic side, the platinum gauze being retained on the acid side. The results are shown in Table 8.

In the third experiment copper was substituted for platinum on the basic side. It was thought that as no acid is ever present on the cathode side of the membrane during dialysis, copper would not be attacked and could therefore be used. The results of this and subsequent experiments have shown that copper is entirely satisfactory on the basic side. In this experiment a trident-shaped copper-wire electrode was substituted on the basic side for the trident-shaped platinum used in the previous experiment. The results are shown in Table 9.

In the fourth experiment the three-wire copper electrode was retained on the basic side. As the three-wire platinum electrode is less expensive than the platinum gauze, it was thought that it might be possible to substitute the three-wire platinum electrode for the platinum gauze and thus further reduce the cost of the equipment necessary. The results of the experiment with this substitution are shown in Table 10.

In the fifth experiment a piece of copper gauze large enough to cover the inner area of the outer chamber was substituted for the three-wire copper electrode on the basic side. This substitution was found to be very satisfactory, having quite an effect on the rate of dialysis,

TABLE 8

Results With Cathode of Three-wire Platinum and Anode of Platinum Gauze.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	0.30	19	0.37	6.76
9	0.20	21	0.17	3.94
21	0.19	19	0.17	2.88
33	0.16	20	0.12	1.35
45	0.10	19	0.11	0.59
		Total	0.93	15.51

TABLE 9

Results With Cathode of Three-wire Copper and Anode of Platinum Gauze.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	0.70	27	0.45	7.79
9	0.20	20	0.14	3.87
21	0.30	20	0.54	2.41
33	0.12	17	0.10	0.73
45	0.05	17	0.06	0.42
		Total	0.89	15.22

T A B L E 10

Results With Cathode of Three-wire Copper and Anode of Three-wire Platinum.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	0.56	26	0.20	6.17
9	0.25	21	0.20	3.13
21	0.28	23	0.26	3.54
33	0.20	20	0.20	1.57
45	0.18	21	0.17	0.65
		Total	1.03	15.06

which will be discussed later. The results of this run are shown in Table 11.

In the sixth experiment, the electrodes used were copper gauze on the basic side as used in the previous experiment and platinum gauze on the acid side as used in the first experiment. The results are shown in Table 12.

Discussion

The various effects produced by the different electrodes described in these experiments are brought out in Figure XVI. It is evident that the use of the copper gauze on the basic side gave the greatest rate of dialysis of any of the combinations tried. The increase in rate over that where platinum gauze was used on both sides is thought to be due to the fact that the copper gauze covered all of the area in the cell, while the platinum gauze, being smaller, did not. This combination seems to be the best available, although a slight reduction in cost can be secured by the use of a trident-shaped platinum electrode instead of the platinum gauze on the acid side. This substitution slows down the rate somewhat, although not seriously. This latter combination seems to be as effective in removing bases as the two platinum gauze electrodes. The other combinations tried all decreased the rate of

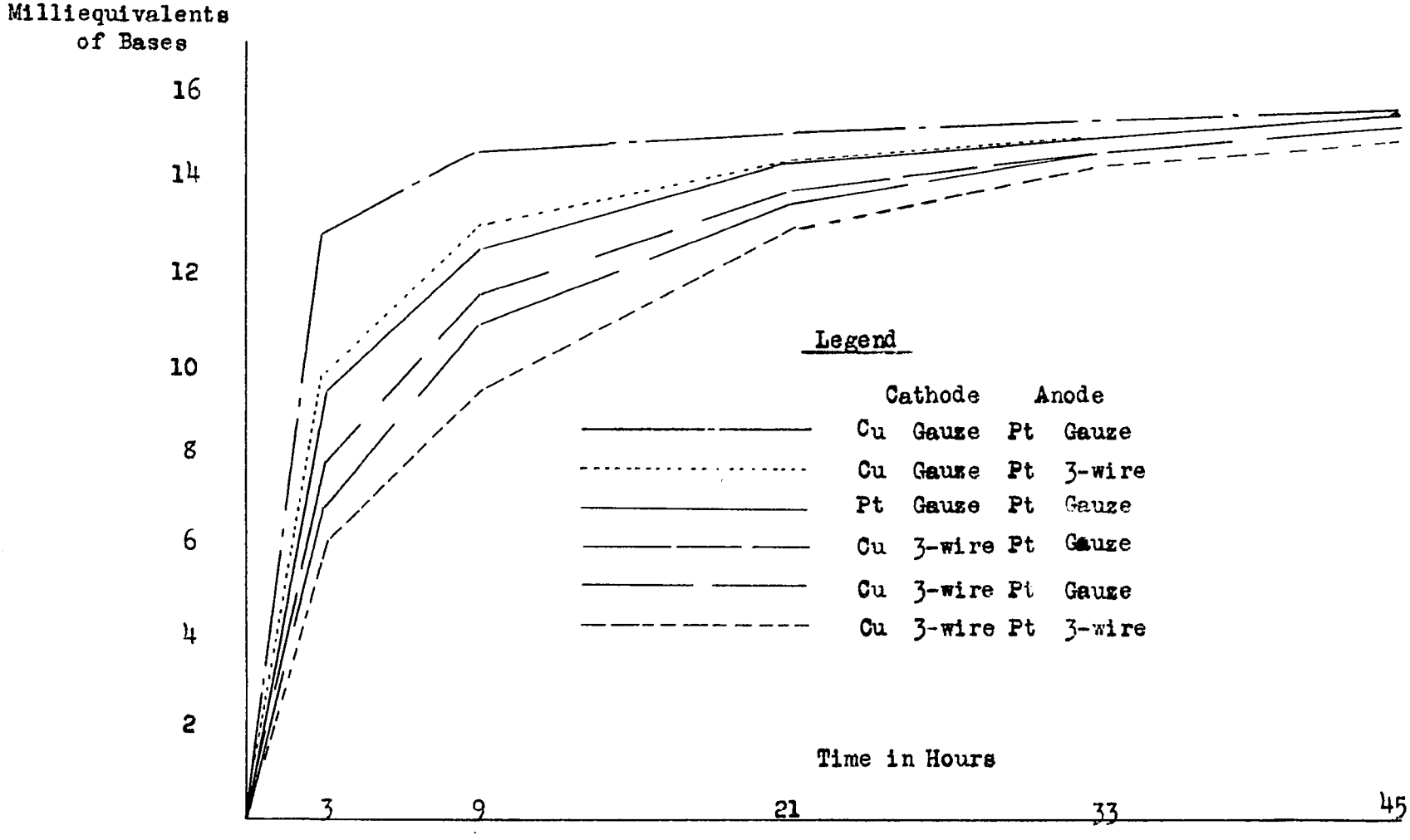

Figure XVI. Results with Various Electrodes

TABLE 11

Results With Cathode of Copper Gauze

and Anode of Three-wire Platinum.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	0.65	28	0.52	9.52
9	0.28	21	0.14	3.54
21	0.16	20	0.19	1.55
33	0.20	20	0.16	0.49
45	0.17	20	0.12	0.31
		Total	1.13	15.41

T A B L E 12

Results With Cathode of Copper Gauze

and Anode of Platinum Gauze.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	1.00	29	0.63	12.65
9	0.17	18	0.18	2.06
21	0.20	19	0.16	0.56
33	0.05	18	0.13	0.23
		Total	1.10	15.50

dialysis, the combination of a three-wire copper and a three-wire platinum electrode being the slowest.

Figure XVI also shows that the end-points all approach the same line and that the total amounts of bases obtained would be the same regardless of which combination of electrodes was used. These and other experiments all show that for any one soil the quantity of bases extracted is very definite and is not affected by the manner of extraction.

If some material could be found which could be substituted for platinum on the acid side, then platinum could be eliminated altogether and the initial cost of an electrodialyzing setup would be materially reduced. A review of the literature showed that some form of carbon had been used for this purpose. A sheet of carbon 1/4 inch thick was obtained from which an electrode was cut which had the same dimensions as the copper gauze described previously. As can be seen from Table 13, the rate of dialysis was very satisfactory and the total amount of bases agreed very closely with the amounts obtained by the use of other electrodes.

However, on the acid side, it was found that the solutions became very turbid, practically black, on account of the decomposition of the carbon under the influence of the electric current. Titration of the acid side was im-

TABLE 13

Results With Cathode of Copper Gauze and Anode of Carbon.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	1.80	34	No titration for acids on account of turbidity of solutions due to colloidal carbon	11.03
9	0.75	30		3.03
21	0.34	22		1.15
33	0.25	21		0.09
45	0.16	20		0.07
			Total	15.37

possible under this condition. The indications are that carbon could be used on the acid side if only base exchange is to be studied. Although the carbon is attacked, an electrode 1/4 inch thick would last some time and, as it is comparatively inexpensive, could be easily replaced.

In correspondence with the research laboratories of the General Electric Company, they suggested the possible use of tungsten or molybdenum in place of platinum. They very kindly furnished tungsten and molybdenum electrodes of the same size as the carbon described in the foregoing experiment. The results with the use of tungsten are shown in Table 14.

The table shows that in the time allowed, 45 hours, the end-point for the bases was not reached; while on the acid side, the titration was about twice as high as where platinum was used. The electrode was weighed both before and after dialysis and was found to have lost between 0.5 and 0.6 gram in weight. The first change on the acid side was rather turbid, the suspension being yellowish-white in color. In all the acid dialysates some sediment was present. No chemical tests were made, but it is known that tungsten will form compounds with acids, phosphoric acid being most active. Although tungsten is almost entirely acid resistant, it is apparent that under the action of the electric current undesirable reactions took place.

TABLE 14

Results With Cathode of Copper Gauze

and Anode of Tungsten.

Time in hours	Ammeter reading in amperes	Temperature in degrees C.	M. E. acids	M. E. bases
3	0.20	20	0.74	3.82
9	0.14	19	0.24	2.31
21	0.21	19	0.50	3.07
33	0.15	18	0.41	2.29
45	0.20	19	0.33	0.97
		Total	2.22	12.46

Molybdenum was found to be much more seriously affected. The decomposition was so rapid in this case that the dialysis was abandoned after only a short time as it was evident that the results would be unsatisfactory.

Summary

1. Results of experiments are given in which different combinations of platinum, copper, carbon, tungsten, and molybdenum are used as electrodes.

2. A copper gauze electrode on the basic side and a platinum gauze electrode on the acid side gave the greatest rate of dialysis.

3. Platinum was found to be the best material for the acid side, while carbon, tungsten, and molybdenum proved to be unsatisfactory.

4. A copper gauze electrode on the basic side and a three-wire platinum electrode on the acid side was the least expensive combination that gave satisfactory results.

III. REACTIONS OF ELECTRODIALYZED HUMUS AND BENTONITE: APPLICATIONS OF THE METHOD.

Introduction

In the electrodialysis of different soils it was noticed that the amounts of bases extracted varied considerably without any apparent reason. As an example of this variation in base exchange content, the results from the electrodialysis of four different soils are given in Table 15.

Twenty-three milliequivalents of bases were extracted from a virgin Carrington loam, 16 from a Tama silt loam, and 12 from a Clinton silt loam. All three soils had an acid reaction: the Tama silt loam had a pH of 5.4, the Carrington loam a pH of 5.7, and the Clinton silt loam a pH of 6.0.

Considering the texture of the soils and their reaction, it would be expected that the Clinton silt loam would contain the largest amount of replaceable bases, yet, it has the smallest amount, almost half of that of the virgin Carrington loam which is more acid and lighter textured. The Tama silt loam, also, gave a larger amount of extracted bases than the Clinton. The texture of these

TABLE 15

Milliequivalents of Bases Extracted from Different Soils.

Hours of electrodialysis		M. E. Clinton silt loam	M. E. Tama silt loam		M. E. Carrington loam (virgin)
3		9.72	12.45		
6					7.65
9		1.59	3.00		
18					7.85
21		0.85	0.45		
24					5.13
30					1.74
33		0.31	0.29		
42					1.00
45		0.23	0.25		
54	Total	12.70	16.44		0.29
66					0.13
				Total	23.79

two soils was the same but the Tama was more acid than the Clinton. The only apparent reason that would account for the difference in the base exchange content of these three soils when their texture and reaction were considered was the differing quantity of organic matter contained in them. The virgin Carrington loam was the coarser textured with the highest amount of exchangeable bases. Judging by appearances this soil seemed to be the highest in organic matter of the three while the Clinton with the lowest amount of replaceable bases was also lowest in organic matter.

It is generally accepted that base exchange reactions take place in the colloidal complex. The part played in these reactions by the organic and inorganic constituents of the soil complex has not been fully established. The following work was undertaken to throw some further light on this soil problem.

Historical

Gedroiz (11) considers that humus takes part in base exchange reactions. He treated soil with 10 percent hydrogen peroxide and warmed it between 30° and 40°C. to rid it of organic matter. Before treatment the replaceable calcium was 0.810 and after treatment 0.056 percent. Experiments were also carried out on clays freed of organic matter. While he does not consider the evidence conclusive,

he believes that the organic matter and inorganic colloids take part in base exchange reactions.

Hissink (14)(15) in his work on the application of lime to soils found that the adsorptive capacity of humus to clay substance was in the ratio of 176 to 1225. The figures were obtained by dividing the humus and clay substance by the total bases the materials were capable of holding. Thus, the humus substance has a far greater adsorption capacity than the clay substance, about 7 to 1. Hissink considers the figures an approximation only as the humus soils were not free of clay nor were the clay soils entirely free of humus.

Burgess and McGeorge (4) do not consider that humus has a true base replacement capacity. In their opinion the so-called organic humates have no capacity for base replacement other than a variable physical adsorption. From their experiments they conclude that treating the soil with hydrogen peroxide has an injurious effect on the base exchange reactions of the zeolite content.

Kerr (21) finds organic matter to possess a high base exchange capacity. The total exchange capacities of three soils were determined before and after treatment with hydrogen peroxide. He found the adsorption capacity of these soils due to organic matter to be from 7 to 28 percent.

The review of literature shows no general agree-

ment of ideas regarding the function of organic matter in base exchange reactions.

Experimental

In this work the reactions of humus were compared with that of bentonite. Bentonite was chosen because it is a naturally occurring soil colloid, free of organic matter, with a high base exchange capacity as compared with other soil colloids.

The humus used was extracted from a peat soil made up of 50 percent organic matter. The peat was washed with 1 percent HCl till the percolate was free of calcium and then washed with water till free of chlorides. The washed humus was transferred to a beaker and 4 percent ammonia added. After standing for 15 hours, the supernatant liquid was poured off and passed through a Pasteur-Chamberland filter. The material thus secured varied in ash content somewhat but some of it had an ash content as low as 1 percent after being electrodialyzed for several weeks.

The colloidal bentonite used was of the material remaining in suspension after four months standing of a dispersion of 60 grams of bentonite in 16 liters of distilled water.

The adsorptive capacity of humus and bentonite.

A T - S according to Hissink (13) was run on bentonite and humus. The bentonite had been electrodialyzed to a pH of 2 and the humus to a pH of 2.37. After electrodialysis the material was dispersed and 10 cc of the resulting suspension placed in Erlenmeyer flasks. Varying amounts of $Ba(OH)_2$, 0.0522 N for the bentonite and 0.1317 N for the humus, were added. The bentonite suspensions were made up to 50 cc and the humus to 70 cc by additions of water. Three runs were made on the humus before enough $Ba(OH)_2$ of the proper strength was found to get a straight line from the plotted results. The results figured on the basis of 10 grams dry weight of bentonite and humus are shown in Figures XVII and XVIII.

The humus took up 162 milliequivalents of $Ba(OH)_2$ as against 22 for the bentonite, a ratio of about 7 to 1.

Reactions of electrodialyzed humus.

Humus was extracted in the usual manner, dried on the steam bath, electrodialyzed, and dried again. The ash content was determined on a portion of it and found to be 5 percent. The dried humus was washed with a solution saturated with calcium chloride till the percolate coming through had the same reaction as the calcium chloride solu-

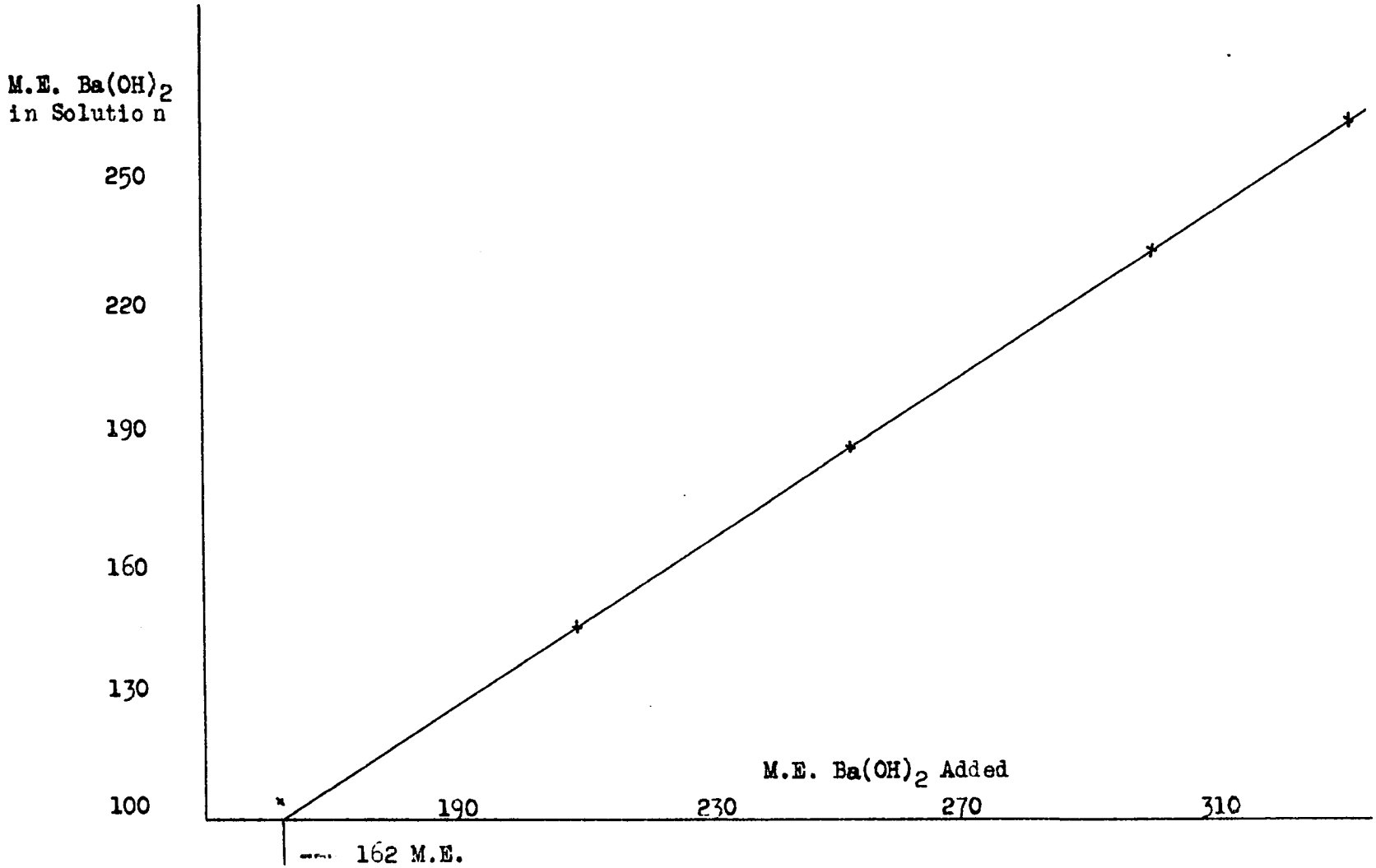

Figure XVII. T-S for 10 Grams Humus

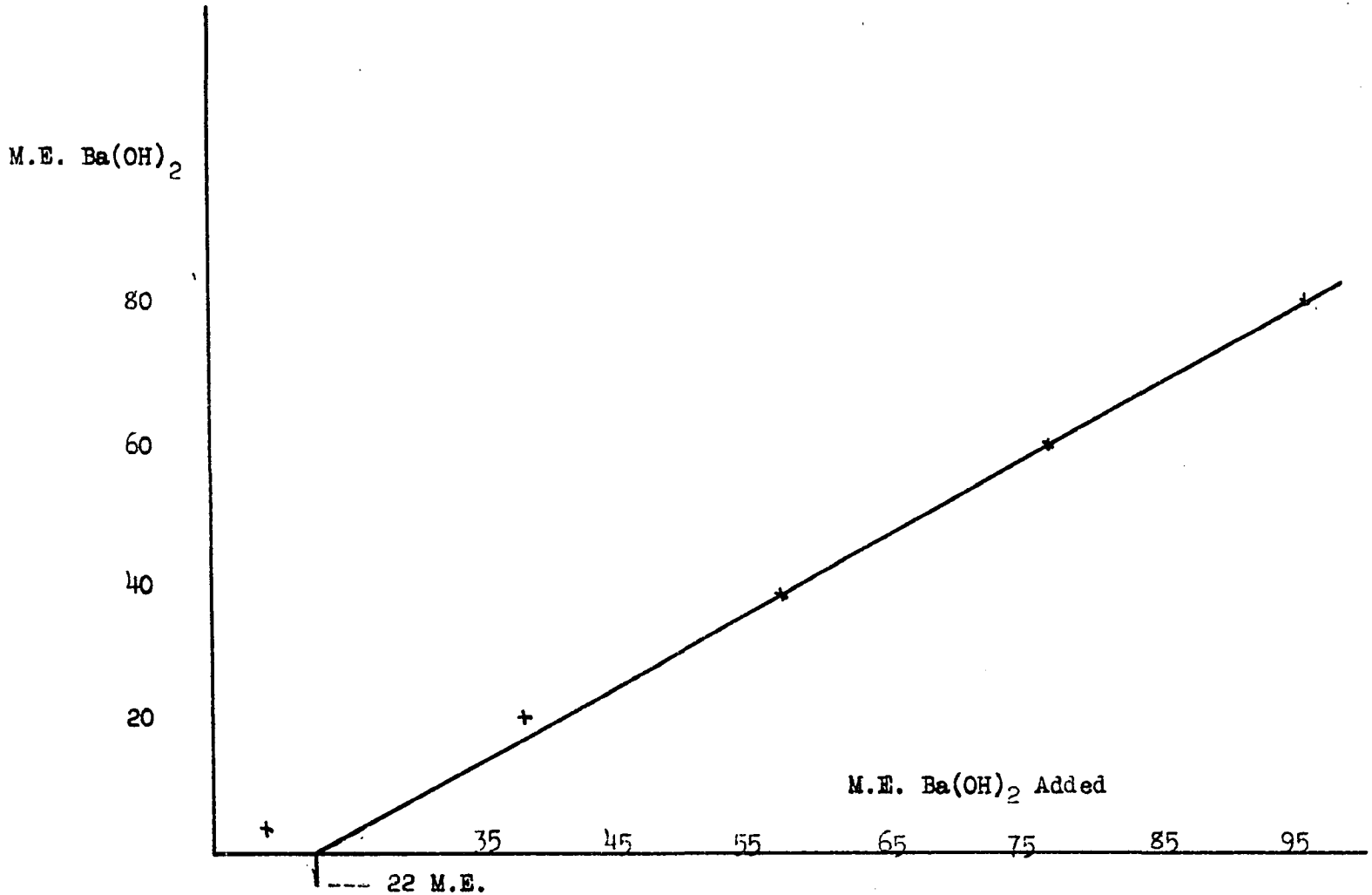

Figure XVIII. T-S for 10 Grams Bentonite

tion with which the material was being washed. The material was washed free of chlorides and the reaction determined. Before treatment with calcium chloride the reaction was 3.15, after treatment 4.78.

Another portion of humus was treated as before except that it was not dried down at any time. Before being treated with calcium chloride it had a pH of 2.67, after treatment 8.2.

Electrodialyzed humus seems to be less active chemically after it has been dried down. It dries down into a coal-like substance that has no visible solubility in water even after standing for several weeks. Some dried electrodialyzed humus was treated with a potassium chloride solution. There was no apparent reaction with the cold solution and little apparent reaction after boiling for an hour. Yet, electrodialyzed humus, undried, treated with a potassium chloride solution became so dispersed no available filter would hold it. The dried electrodialyzed humus reacted readily enough with potassium hydroxide.

There is some evidence in the literature that humus is considered as being rather inert chemically. The word "humus" probably does not have the same meaning to all soil workers. The material itself can easily vary considerably because of the different conditions under which it is formed. Lack of agreement on what constitutes humus and the probable variability of the material could account

for the variable results reported.

The humus material worked with in these experiments did not appear to be inert, some evidence of which has already been presented. In the electrodialyzing cell, the material had a negative charge as it collected on the positive membrane. Photographs were made of membranes used in the electrodialysis of humus. They are shown in Plate 1.

The upper picture is that of the membrane on the positive side. It shows the humus adhering to the membrane while the lower picture of the negative membrane shows it to be free of humus.

Some electrodialyzed humus, pH 3.7, was titrated with 0.1062 N sodium hydroxide. The curve plotted from the results is shown in Figure XIX. The shape of the curve indicates that the humus material probably contained a mixture of acids, although a divalent acid could give the same type of curve.

Titrations of electrodialyzed humus were made with a conductivity apparatus, using calcium hydroxide, aluminum hydroxide, and ferrous oxide. The humus had a pH of 3.6 at the start of the titration. The dry weight of the humus used was 0.328 grams. The amounts of bases used are shown in the figures. The results are shown in Figures XX, XXI, and XXII.

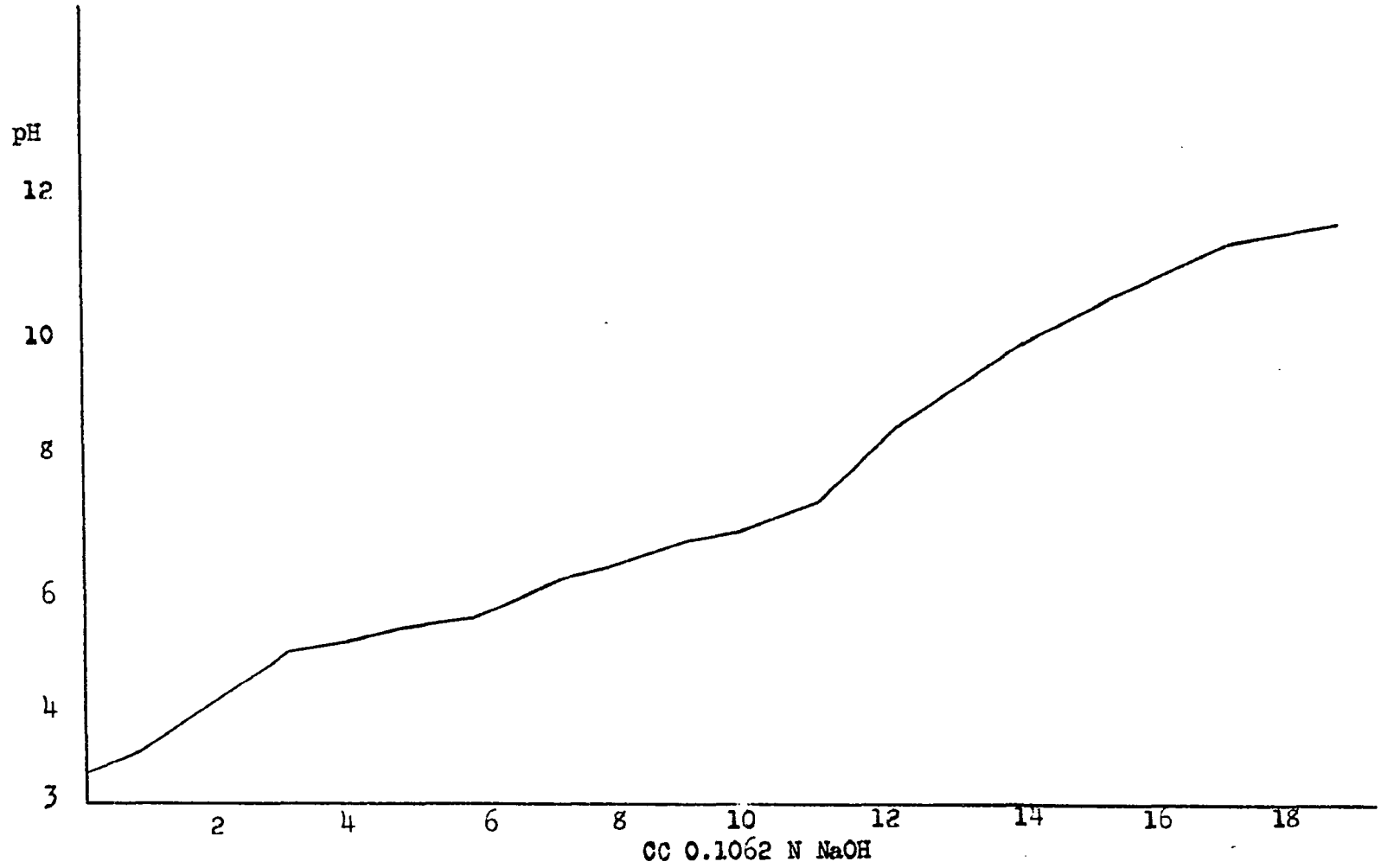

Figure XIX. Titration of Humus with NaOH

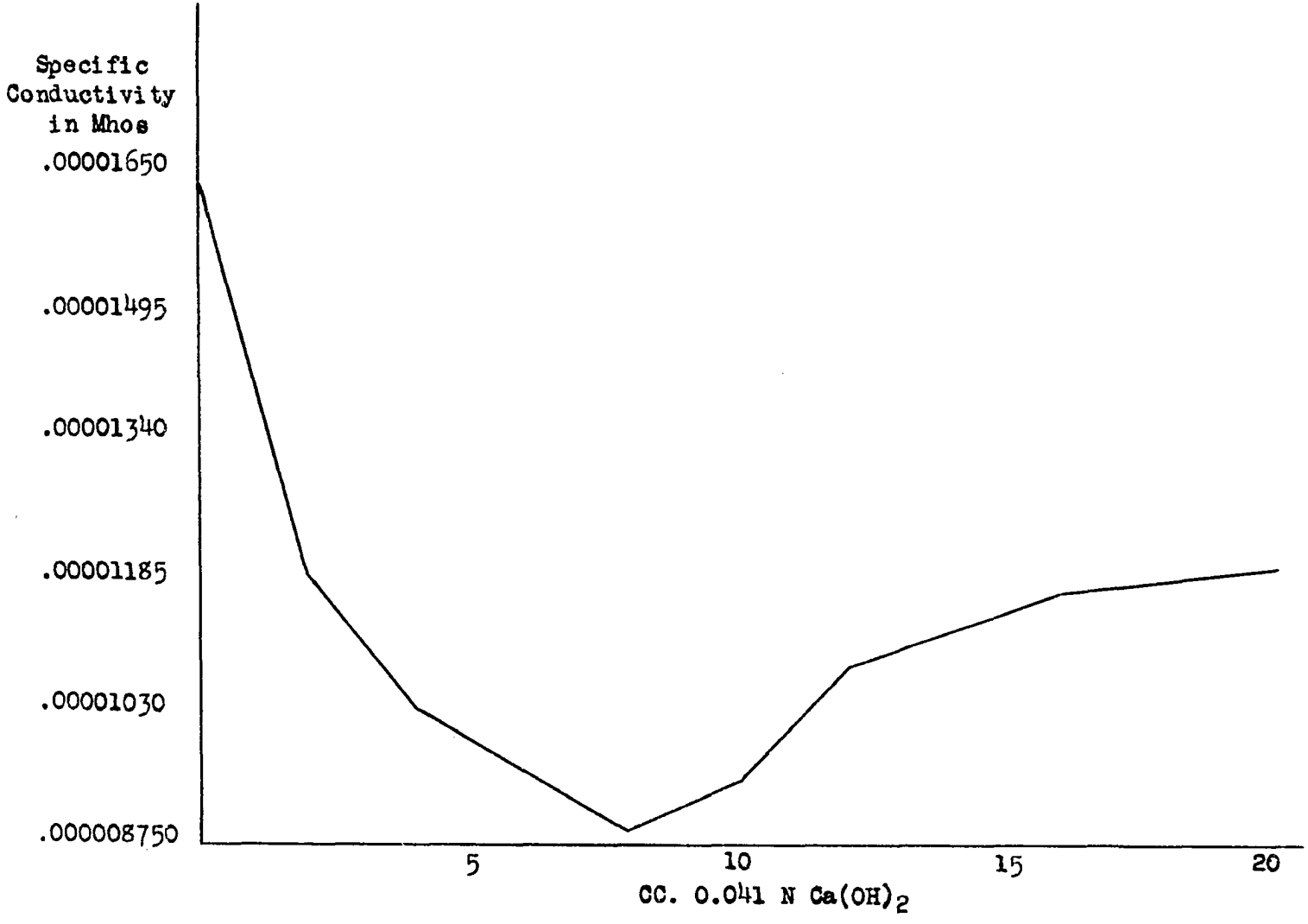

Figure XX. Conductivity Titration Humus and $Ca(OH)_2$

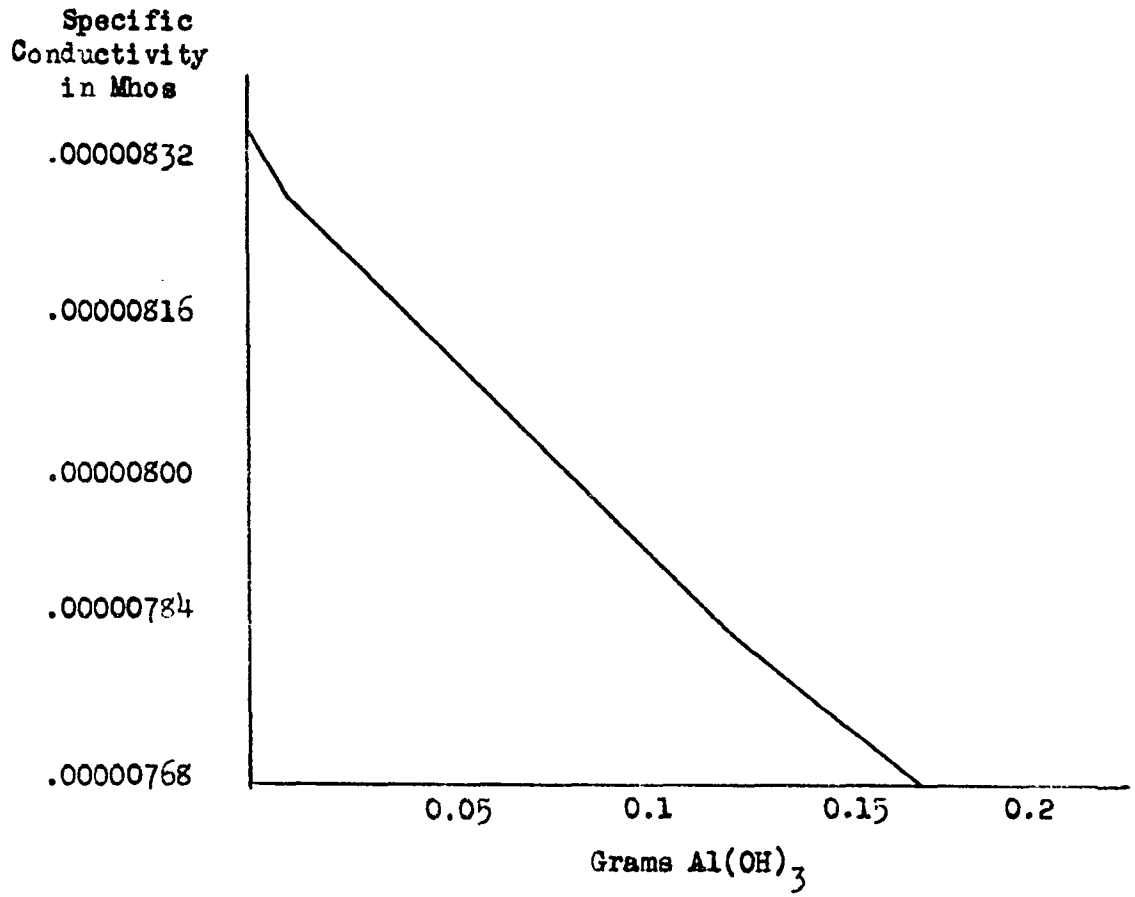

Figure XXI. Conductivity Titration Bentonite and $Al(OH)_3$

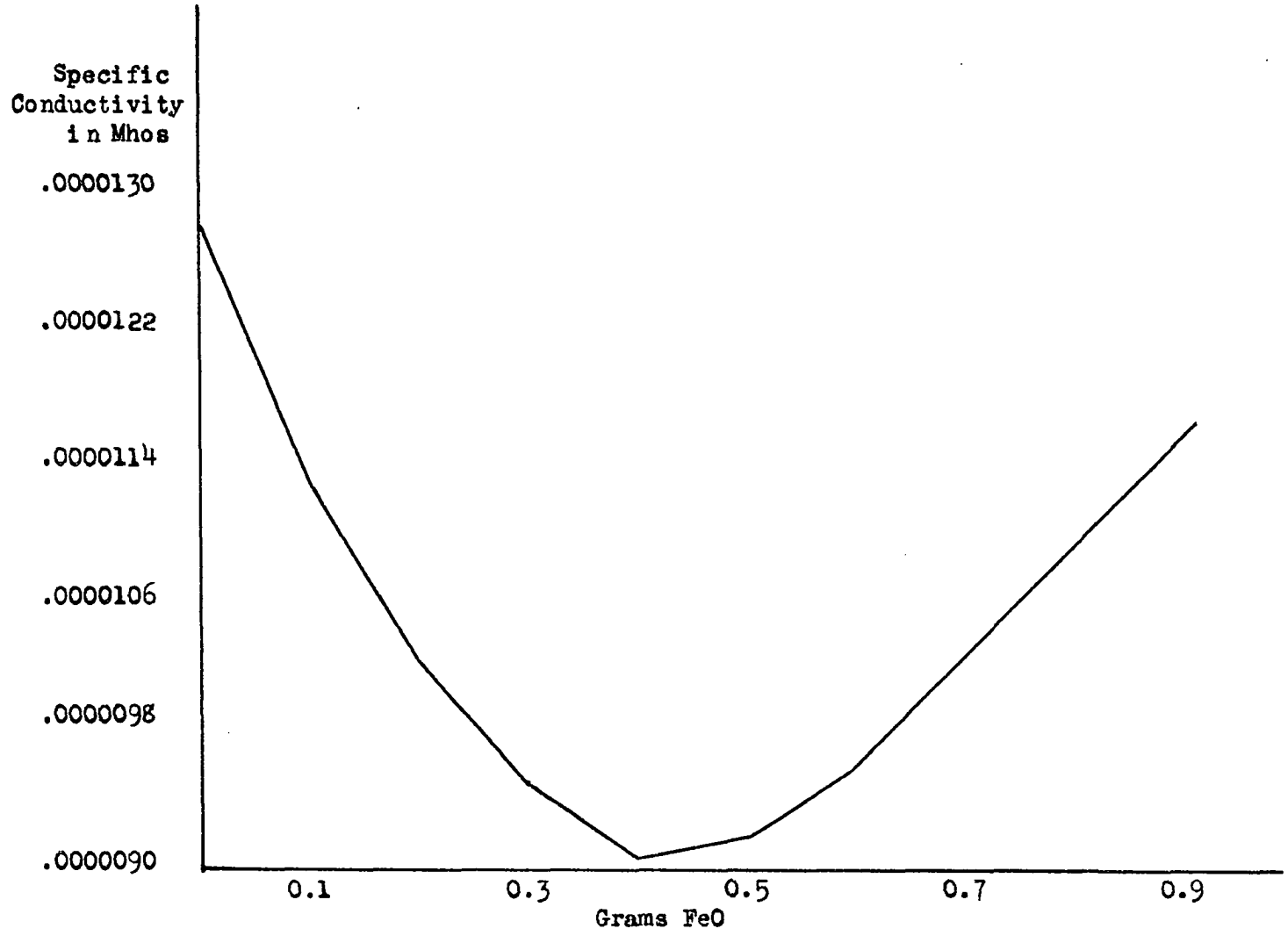

Figure XXII. Conductivity Titration Humus and FeO

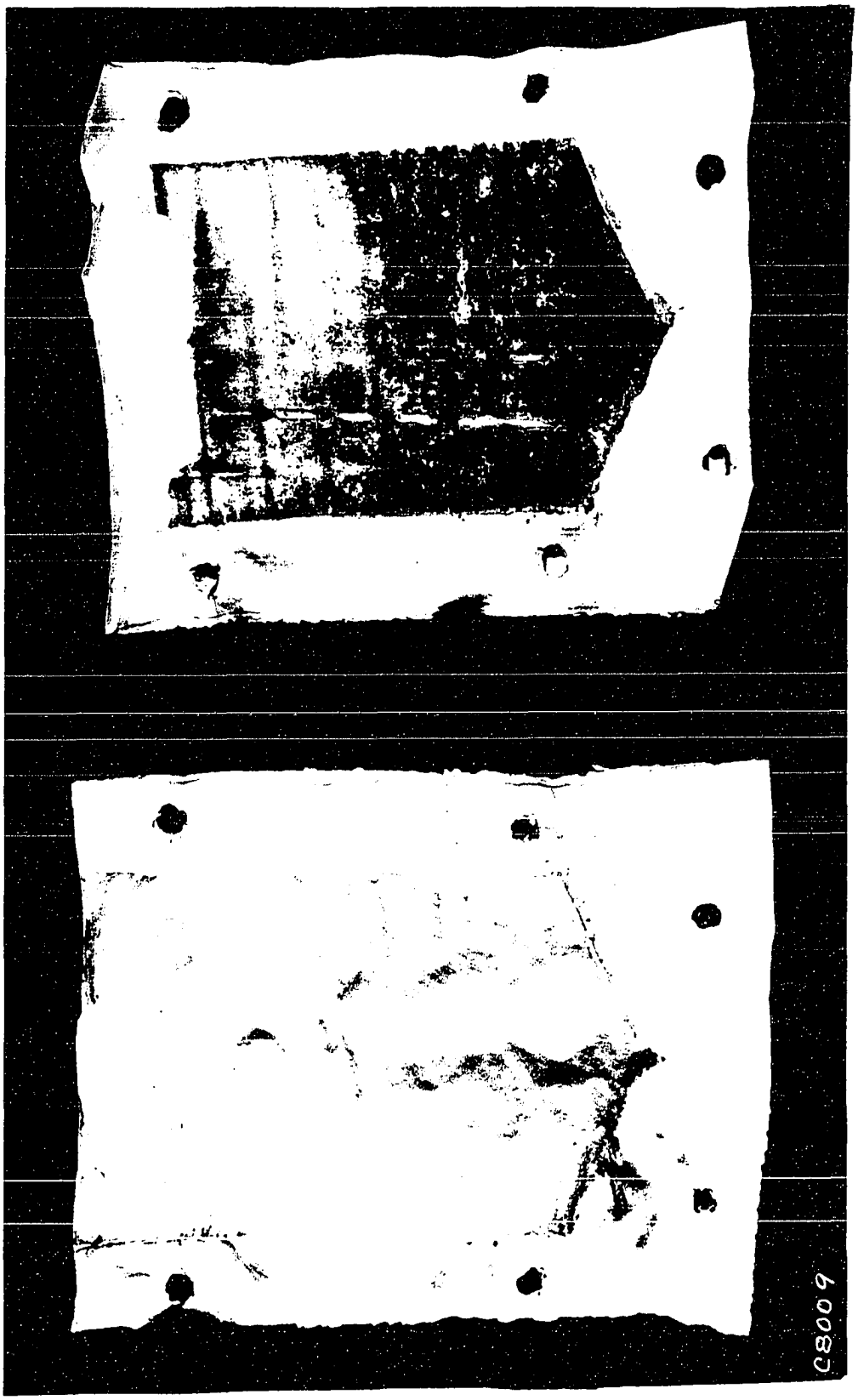

Plate I Upper Membrane Positive Side; Lower, Negative Side

The first reading was that of the humus itself. As the H-ion is the fastest ion, the first reading is due mainly to that ion. When a base is added and reaction takes place, some of the H-ions are neutralized, causing the conductivity to drop. The result is a downward trend in the plotted curve. The next fastest ion to the H-ion is the OH-ion. The curve takes an upward trend when base is added after neutralization has taken place. The shapes of the curves indicate that calcium hydroxide, ferrous oxide, and aluminum hydroxide reacted with the humus. The titration with aluminum hydroxide was not completed as interest was primarily in whether or not aluminum would combine with humus.

An attempt was made to form an aluminum humate, using electrodialyzed humus and aluminum chloride. The experiment was unsuccessful. The reason was evident after the reaction of the aluminum chloride had been taken. Some reactions of aluminum chloride are given in Table 16.

The results in Table 16 show why aluminum humate was not formed with the use of aluminum chloride. The H-ion is more abundant in solutions of this salt than in the suspensions of electrodialyzed humus.

Reactions of electrodialyzed bentonite.

A portion of the colloidal bentonite previously mentioned was electrodialyzed for several days, removed

TABLE 16

Some Reactions of Aluminum Chloride.

Normality	pH
0.001	4.31
0.010	3.75
0.100	3.65
1.000	3.10

from the cell, and dispersed in a small quantity of water. The resulting suspension had a pH of 2.0. Ten cc of this suspension were diluted to 100 cc, ten cc of this new suspension diluted to 100 cc, etc. The dilutions and resulting pH are given in Table 17.

The reaction drops off rather sharply after the second dilution. However, considering the fact that this material is a colloidal suspension and not a substance in solution, the acidic properties are rather marked.

Electrodialyzed bentonite was titrated in a conductivity apparatus with sodium hydroxide, ammonium hydroxide, calcium hydroxide, aluminum hydroxide, and ferrous oxide. The aliquots of bentonite contained 0.283 grams dry weight of bentonite which had a pH of 3.34 at the start of the titration. The results are shown in Figures XXIII, XXIV, XXV, XXVI, and XXVII.

The curves in the figures indicate that bentonite reacted with ammonium, sodium, and calcium hydroxide and ferrous oxide but did not react with aluminum hydroxide.

Discussion

One portion of humus was electrodialyzed to a pH of 1.5, giving a reaction equal to a 0.0316 N acid. The lowest reaction secured with bentonite was a pH of 2 equal to a 0.01 N acid. The humus gave an acid reaction three

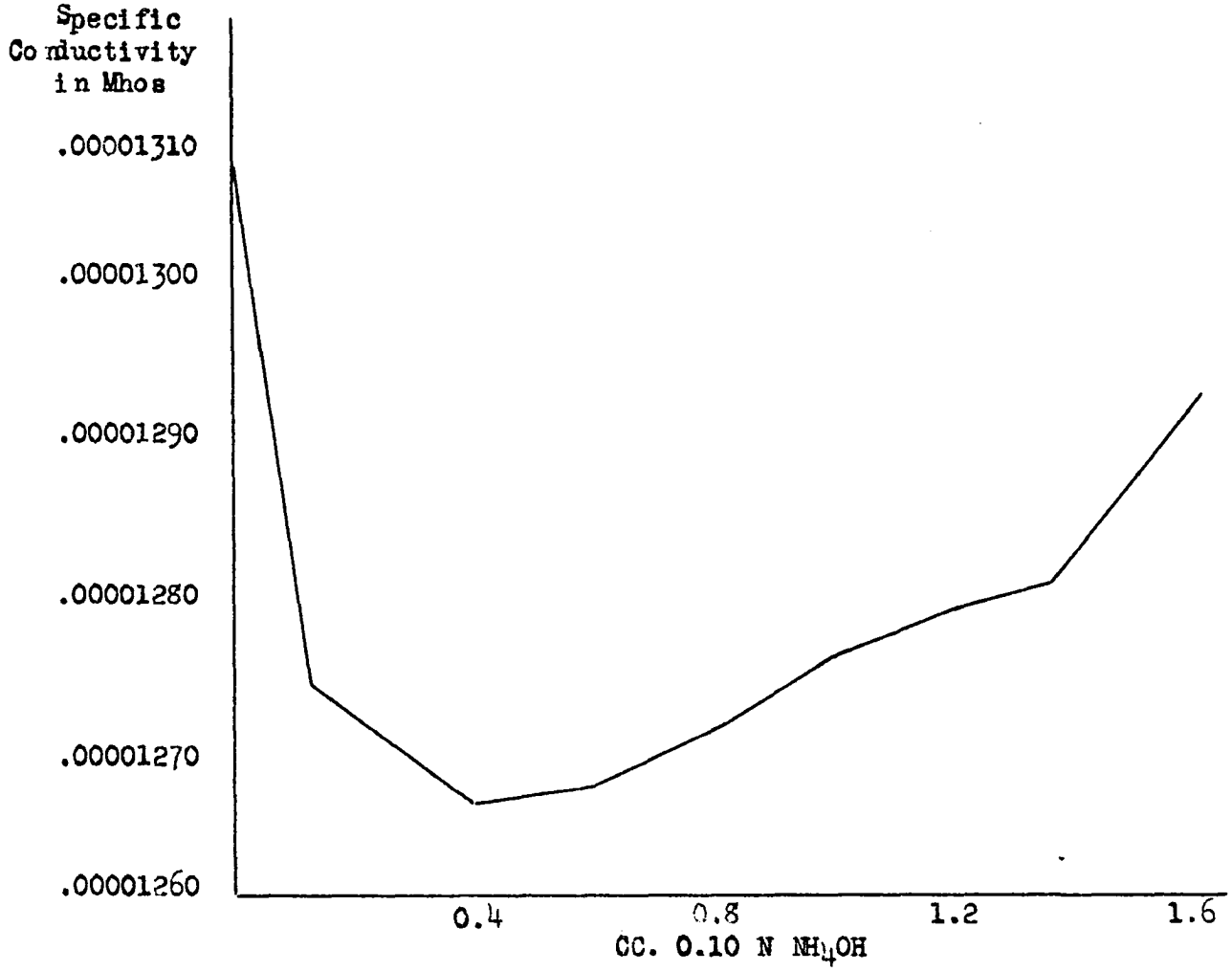

Figure XXIII. Conductivity Titration Bentonite and $NH_4O\ddot{H}$

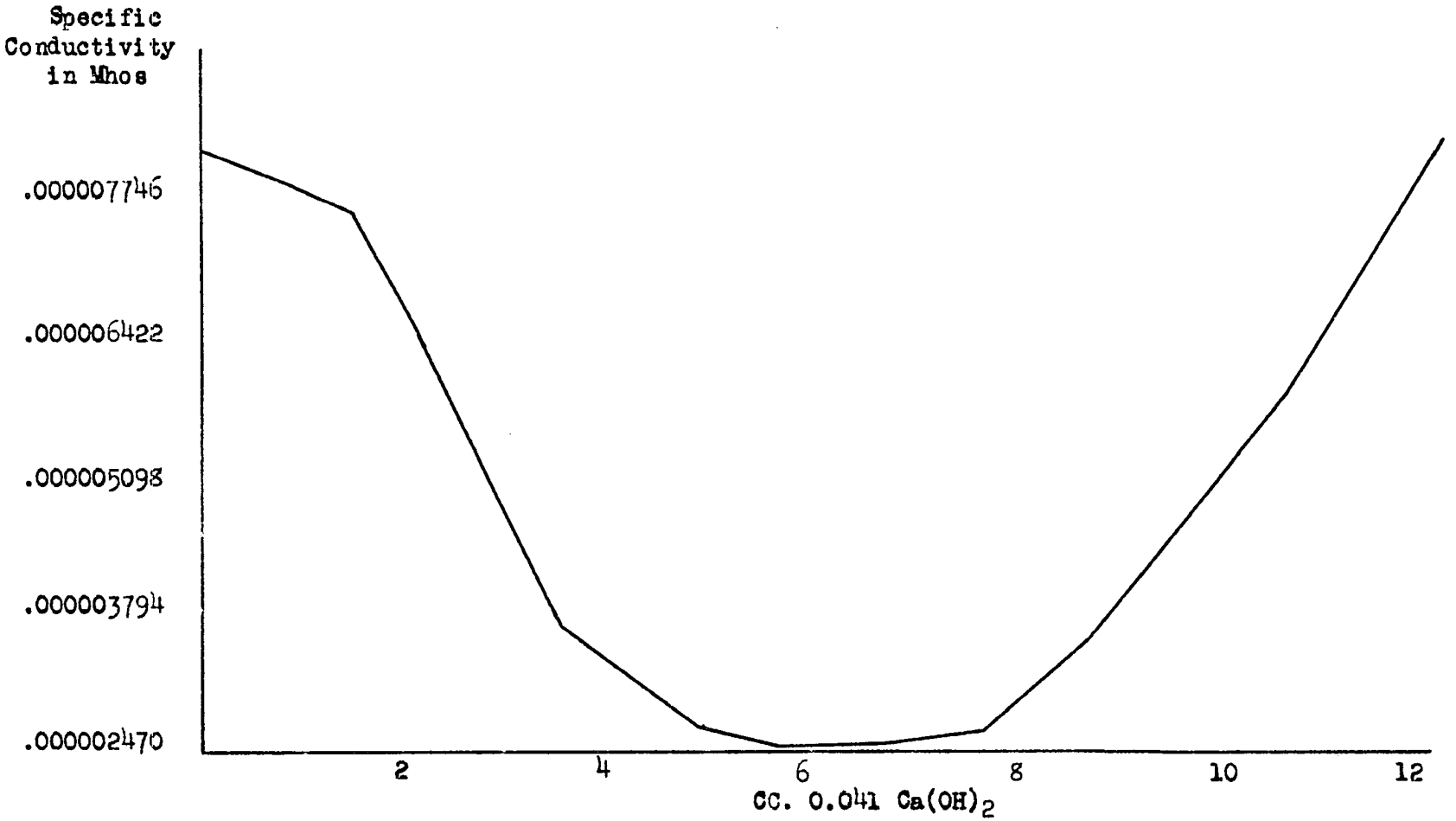

Figure XXIV. Conductivity Titration Bentonite and $Ca(OH)_2$

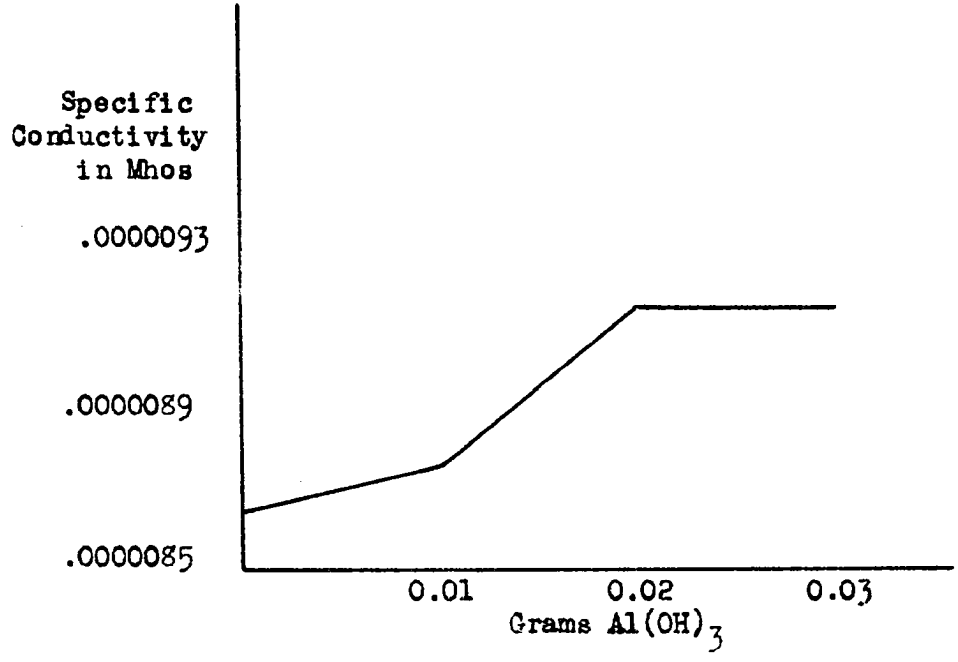

Figure XXV. Conductivity Titration Bentonite and $Al(OH)_3$

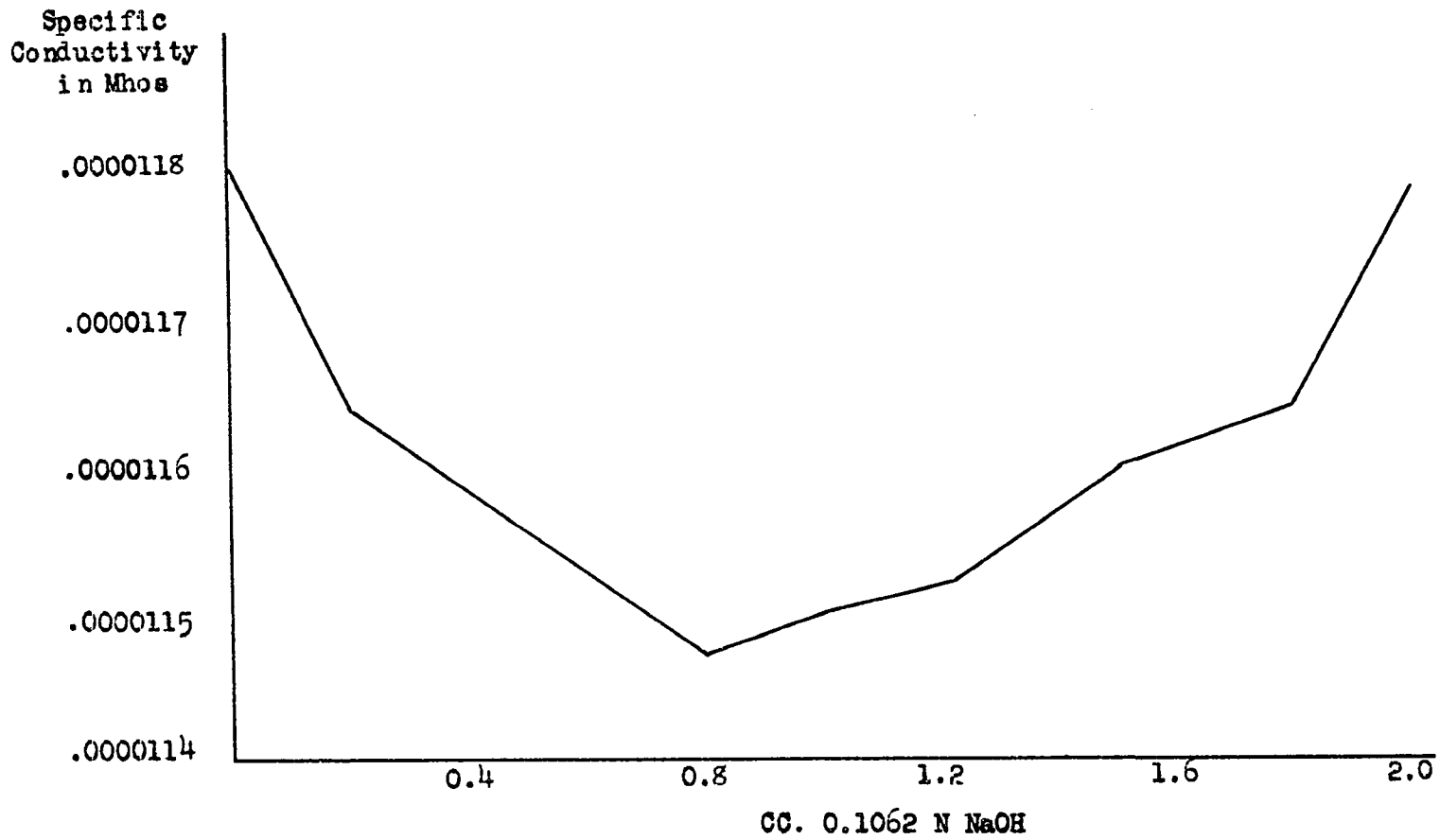

Figure XXVI. Conductivity Titration Bentonite and NaOH

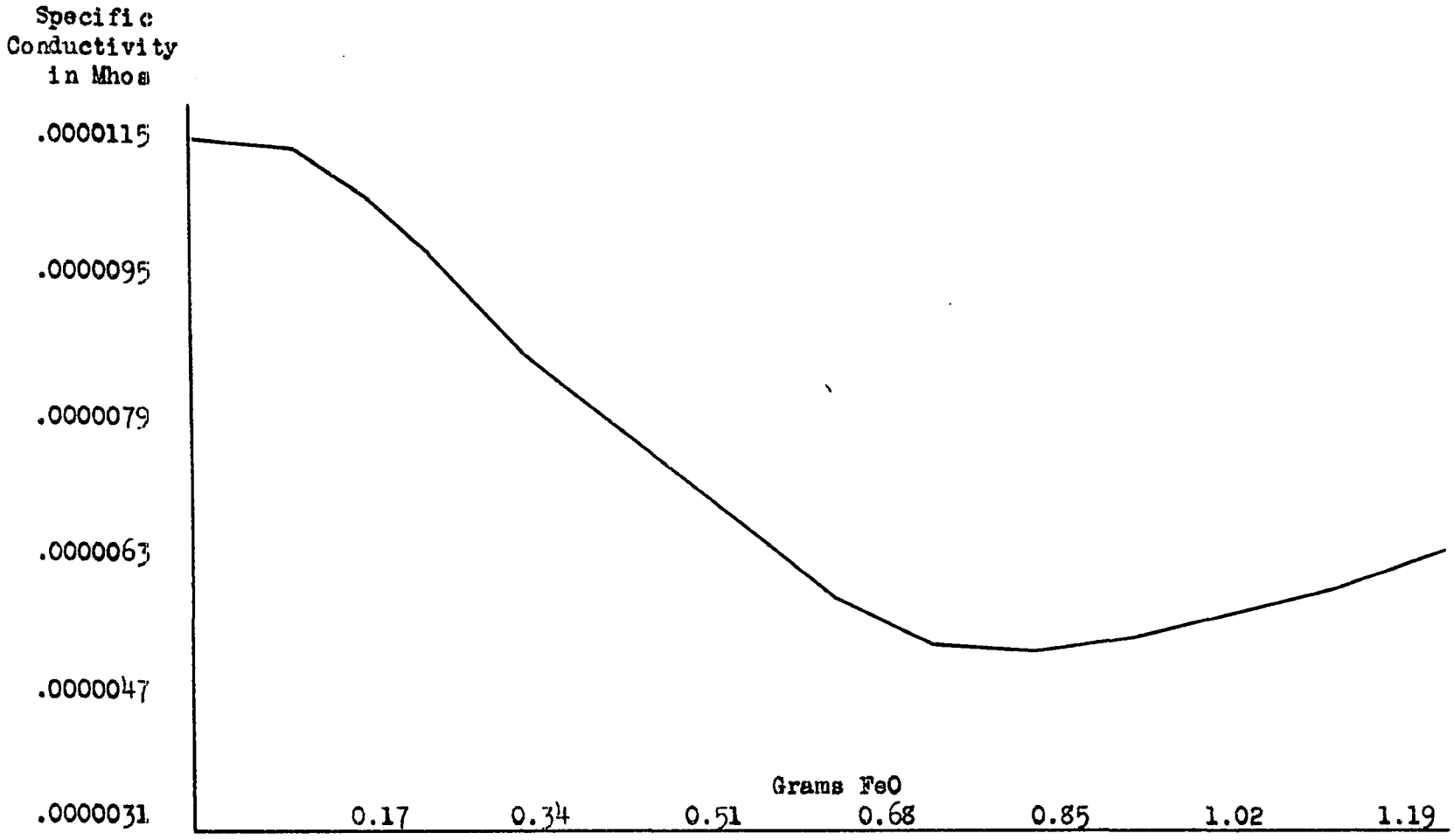

Figure XXVII. Conductivity Titration Bentonite and FeO

TABLE 17

Reactions of Electrodialyzed Bentonite.

Dilution	pH
Original material	2.00
1st dilution	3.40
2nd "	5.82
3rd "	6.53
4th "	6.84
Distilled water	6.84

times as strong as the colloidal bentonite.

The humus worked with in the T - S experiment had seven times the adsorptive capacity of colloidal bentonite. The portion of humus on which this experiment was made had an ash content of 1 percent after it was electrodialyzed. If the organic matter in this sample was inert and the reaction due solely to a possible adhering zeolite, this zeolite would have had a base exchange capacity seven hundred times that of the colloidal bentonite. It is doubtful if such a zeolite exists. Mattson (27) found bentonite to be a material with a high ratio of SiO_2 to sesquioxides and to have a base exchange capacity equal to that of any material with which he worked.

It is evident that before a base exchange reaction can take place, a base must be present in the exchange complex. Sodium, potassium, calcium, and magnesium have long been considered to take part in base exchange reactions. The results in this work indicate that iron and aluminum could possibly take part in base exchange reactions as iron and aluminum humates were formed and also an iron "clayate".

Summary

1. Humus was found to have an adsorptive capacity seven times that of bentonite.

2. Humus was found to react with aluminum and calcium hydroxide and ferrous oxide.

3. Bentonite was found to react with ammonium, calcium, and sodium hydroxide, and ferrous oxide.

4. Bentonite did not react with aluminum hydroxide.

Application of Electrodialysis

Analysis of the Dialysates from Two Acid Soils.

A Tama silt loam and a Clinton silt loam, two acid soils, were electrodialyzed and changes made of the dialysates at 3, 6, 12, 12, and 12 hour intervals. Analyses were made of the bases and phosphorus present in the dialysates. The results are shown in Tables 18, 19, 20 and 21.

In computing milliequivalents iron and manganese were both given a valence of two as they were thought to be more apt to occur at this valence than at a higher one, especially as they were in the presence of organic matter.

Calcium was the most abundant element in the dialysates of both soils. The largest amount, 72 and 80 percent, of this element came out in the first three hours of electrodialysis. The amounts in subsequent changes decreased rapidly. The amount of magnesium was one seventh

T A B L E 18

Milliequivalents of Bases and PPM of Phosphorus in Tama Silt Loam.

Time between changes	M.E. Ca	M.E. Mg	M.E. Mn	M.E. A_1	M.E. K	M.E. Fe	PPM P
3 Hrs.	6.70	1.17	0.02	0.07	0.06	0.05	3.7
6 "	1.50	0.75	0.12	0.23	0.07	0.10	3.1
12 "	0.50	0.43	0.50	0.14	0.09	0.04	3.0
12 "	0.29	0.15	0.16	0.06	0.11	0.03	2.8
12 "	0.20	0.10	0.09	0.07	0.09	0.03	2.6
Total 45 Hrs.	9.19	2.60	0.89	0.57	0.42	0.25	15.2

TABLE 19

Milliequivalents of Bases and PPM of Phosphorus in Clinton Silt Loam.

Time between changes	M. E. Ca	M.E. Mg	M.E. Al	M.E. Mn	M.E. Fe	M.E. K	PPM P
3 Hrs.	7.61	1.23	0.03	0.03	0.06	0.01	5.80
6 "	0.88	0.96	0.07	0.77	0.09	0.01	5.73
12 "	0.67	0.41	1.00	0.80	0.32	0.02	5.80
12 "	0.20	0.15	0.95	0.15	0.36	0.02	2.50
12 "	0.15	0.06	0.93	0.04	0.22	0.01	1.75
Total 45 Hrs.	9.51	2.81	2.98	1.79	1.05	0.07	21.58

TABLE 20

Percentage of Each Element in Each Change of the Total Amount for that Element Extracted from Tama Silt Loam.

Change	Time between changes	Percent Ca	Percent Mg	Percent Mn	Percent A_1	Percent K	Percent Fe	Percent P
1	3	72.89	45.00	2.24	12.28	14.29	19.96	24.34
2	6	16.34	25.00	13.49	40.35	16.66	40.00	20.39
3	12	5.44	17.30	56.18	24.66	21.42	16.01	19.73
4	12	3.15	5.76	17.98	10.52	25.19	12.00	18.42
5	12	2.17	3.84	10.16	12.28	21.42	12.00	17.10

T A B L E 21

Percentage of Each Element in Each Change of the Total Amount for That Element Extracted From Clinton Silt Loam.

Change	Time between changes	Percent Ca	Percent Mg	Percent A_1	Percent Mn	Percent Fe	Percent K	Percent P
1	3	80.21	43.79	1.00	1.67	5.71	14.28	26.73
2	6	9.23	34.12	2.39	43.03	8.57	14.28	26.55
3	12	7.04	14.59	33.56	44.69	30.40	28.59	26.87
4	12	2.10	5.33	31.84	8.37	34.29	28.59	11.58
5	12	1.57	2.13	31.28	2.23	20.95	14.28	8.10

of that of calcium. The largest amount, 45 percent, was in the first change. Magnesium, also, decreased in subsequent changes. The amounts of iron, aluminum, and manganese followed a general trend of the smallest amount in the first change, increasing amounts in the second and third changes, and decreases in the fourth and fifth changes. Total potassium averaged only 2.5 percent of the total calcium and only 2.4 percent of the total bases extracted. The amounts of phosphorus extracted from the two soils did not vary strikingly either in quantity or rate of extraction.

Reaction of Electrodialyzed Soils

The modified Mattson cell as described previously was used in this experiment. The current was 250 volts. The cooling system kept the temperature of the cell from going above 25°C. The amperage varied with the course of the dialysis but did not rise over two amperes with two cells in use. The results for various changes on a Tama silt loam are shown in Table 22.

The soil used had a pH of 5.7 at the start of the experiment. Three hours of electrodialysis brought the reaction down to a pH of 2.12. Forty-two hours more of dialysis decreased the pH only slightly or to 2.04.

Kelley and Brown (20) report a pH of 4.5 for a soil electrodialyzed five days, Rost (30) reports securing

TABLE 22

Reaction of the Various Changes in the Electrodialysis of a Tama Silt Loam.

Change	Hours between changes	pH
1	3	2.12
2	6	2.10
3	12	2.06
4	12	2.06
5	12	2.04

a pH of 2.94, Wilson (36) a pH of 2.7, and Humfeld and Alben (17) a pH of 2.7. The soil reaction secured by means of electrodialysis depends on many factors, among which are: voltage used, pH of original soil and amount of bases contained therein, amount of soil used, frequency of changes, length of run, and type of cell used. These factors account for the varying end-points reported.

Comeback of pH of Electrodialyzed Soil

Two portions of Tama silt loam and Clinton silt loam were electrodialyzed. One set of the electrodialyzed soils was kept under water through the course of the experiment and the other moistened, allowed to dry out, moistened again, etc. The results are shown in Table 23.

The set that was kept under water apparently reached equilibrium in 60 days at a pH of 4.0. The Clinton that was allowed to dry out reached practically the same end-point. The Tama soil that was allowed to dry out ended with a lower pH than the others. This soil contained more humus than the Clinton. The drying out of the humus, making it less reactive, might account for the lower pH reached by this soil.

T A B L E 23

Comeback of Soil pH.

Time	Set kept in water		Set allowed to dry out	
	Clinton silt loam	Tama silt loam	Clinton silt loam	Tama silt loam
Start	2.49	2.60	2.66	2.31
After 30 days	3.60	3.72	3.57	3.57
" 60 "	4.09	3.99	3.89	3.67
" 90 "	4.08	3.97	3.97	3.67

Electrodialysis of a Basic Soil

A Webster silt loam with a pH of 7.7 was electrodialyzed. The results compared with those secured on an acid soil are shown in Table 24.

The last change of the Webster soil, ending at 225 hours, had as large an amount of bases as the last change of the Clinton soil, ending at 45 hours.

The displacement solution methods now in use on basic soils are not entirely satisfactory as it is difficult to determine what portion of the bases extracted is due to the solubility of carbonates. Electrodialysis does not appear to be a promising method for these soils as carbonates decompose under the influence of the electric current. Also, it takes too long a time to reach the endpoint for the method to be of practical value.

Summary

1. Results of the analysis of the dialysates from a Tama silt loam and a Clinton silt loam are given.

2. The reactions of a Tama silt loam during electrodialysis are listed. The final reaction was a pH of 2.04.

3. The reaction of an electrodialyzed soil came back to a pH of 4.0 in 60 days.

TABLE 24

Results With A Basic Soil Compared

With Results With An Acid Soil.

Hours of electrodialysis		M. E. Clinton silt loam (acid)	M. E. Webster silt loam (basic)
3		9.72	9.52
9		1.59	17.87
21		0.85	14.97
33		0.31	6.17
45		0.23	6.42
57			3.85
69			2.79
81	Total	12.70	2.10
93			1.63
105			1.57
129			1.63
141			1.10
153			0.95
165			1.21
177			0.78
206			0.99
213			0.30
225			0.27
	Total		74.12

4. Application of electrodialysis to basic soils is discussed.

ACKNOWLEDGMENT

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